ELECTROLYTE SOLUTIONS TO IMPROVE THE PERFORMANCE OF ELECTROACTIVE POLYMERS USED IN INFUSION PUMPS

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Abstract

Tucson/San Diego-based company Medipacs, Inc. has developed a novel approach to their infusion pump design: the utilization of electroactive polymer materials to serve as mechanical actuators in portable, disposable infusion pumps. Already in working order, Medipacs' electroactive polymer's design is continually perfected in order to both maximize the polymer's mechanical output as well as uncover the full spectrum of design applications for the polymer. As Medipacs' polymer readily swells while submerged in an electrolyte solution at a low pH, the ions that make up the electrolyte solution are not the only important quality; the concentration of the electrolyte solution is also significant as too high or too low of an electrolyte concentration can hinder polymer expansion. The study at hand investigated not only the cause of a surprising improvement in polymer actuation during the utilization of a new (proprietary) electrolyte over the previously used electrolyte, sodium perchlorate, but also looked to further improve actuation through the investigation of additional electrolytes: citric acid, sodium hydrogen sulfate, and sodium nitrate. A passive swelling test that utilized pH changes to facilitate swelling, and an active swelling test that used an electrical current to facilitate swelling were both used; a polymer known to swell in an alkaline solution was also incorporated into the study for comparison. Preliminary results suggest that an electrolyte solution with many acid-dissociation constants facilitates the greatest swelling of Medipacs' polymer, although more experiments are needed to evaluate the ability to electrochemically control such electrolytes.

1. Introduction

1.1. Smart/Electroactive Polymers Overview

1.1.1. What are smart polymers?

At their most basic form, polymers consist of "monomers," small molecules that are covalently bonded together in repeating segments. Polymers exist in a variety of molecular weights (although they usually have a very large molecular weight) and they can have vastly differing chemical properties. Polymers, most widely known as "plastics," exist in every crack and crevice of the world. They exist in nature; rubber is a polymer made by plants, and DNA, the basis of cellular life, is a polymer made of nucleic acid monomers. They can also exist in a synthetic, human-made form; soda bottles bought in vending machines are made from polyethylene.

Clearly, polymers have played a vital role in society for centuries. Interestingly, however, specific types of polymers over the past twenty years have become increasingly popular for their abilities to expand or contract in response to a stimulus such as heat or electricity: smart polymers. The ability to convert an external stimulus into mechanical energy is particularly useful in many biomedical applications including (but not limited to): tissue engineering, drug delivery, microfluidics, and biosensors (Kumar, et al.)

A great variety of smart polymer applications exists partly due to the smart polymers' ability to be tailored according to their intended use. For example, a polymer used as a tissue engineering scaffold will need to degrade over time, but must be strong enough to withstand the initial implantation stresses. In fact, the number of smart polymer applications grows as more biomedical techniques and devices are created; therefore, as the twenty-first century moves forward, more and more research groups are focusing on studying the abilities of smart polymers to maximize the polymers' potential (Kopecek, et al.; Kumar, et al.)

1.1.2. What are electroactive polymers?

Of all of the potential applications of smart polymers, this report is primarily focused on the properties of smart polymers stimulated by an electric charge, and their use as actuator pumps for biomedical applications; these polymers are known as electroactive polymers (Plata, et al). Electroactive polymers are attractive materials due to their ability to expand from their original shape as well as their low cost (Madden, et al.). In addition, with the advancement in computer technology over the past twenty years, electroactive polymers are rapidly taking an even more important role in research and technology.

1.1.3. Two main electroactive polymer categories: ionic and electronic

Electroactive polymers can be separated into two distinct categories, each with their own set of advantages and disadvantages: ionic and electronic electroactive polymers. Electronic electroactive polymers can expand and contract in air, without needing to be submerged in an electrolyte solution that helps to facilitate ion transport through the polymer (Carpi, 2). Electronic electroactive polymers can also operate at higher expansion/contraction frequencies than ionic electroactive polymers, and are also more efficient than ionic electroactive polymers at converting electrical energy to mechanical energy (Carpi, 2). That being said, the electronic electroactive polymers require a very high voltage in order to produce a strong enough electric field to drive the expansion of the polymer matrix; despite all of the promises of electronic electroactive polymers, their high voltage requirement limits their potential applications. (Carpi, 2; Bar-Cohen, 96). The electronic electroactive polymers are most widely known for their use in piezoelectric applications, as motion sensors or actuators (Bar-Cohen 96).

This particular report is primarily concerned with the ionic electroactive polymer type, which must be submerged inside an electrolyte solution in order to respond to an electric stimulus (Madden, et al.; Carpi, 2). During the application of electricity to the electrolyte solution, ions and/or solvent from the electrolyte solution diffuse into the submerged electroactive polymer's three-dimensional matrix, and swelling of the polymer ensues due to either a repulsion of charges (positive charges repel positive charges, and so on), an influx of water, or both (Carpi, p. 8; Osada et al.)

The ionic electroactive polymer's complexity arises from their extreme variability; the overall properties of ionic electroactive polymers are particularly sensitive to the structure

and composition of the polymer, meaning that even small changes in quantity of the constituents used to form the polymer can cause vast differences in performance (Bar-Cohen, 151).

1.1.4. Material Properties of Ionic Electroactive Polymers

1.1.4.1. Ionic Electroactive Polymer Mechanics

Ionic electroactive polymers are not typically strong enough to carry heavy loads (such as in an artificial muscle fiber application for a prosthetic arm), so they are not usually analyzed for their strength, which depends on the swelling state of the polymer being examined; for example, a polymer that has taken up water and increased in volume to twice its original size will be about half as strong as it was before taking up water (Bar-Cohen 156, 157).

1.1.4.2. Cross-Link Density

The degree of polymer cross-linking (the relative number of bonds formed within the polymer matrix that link polymer chains together) is an important consideration for chemical ionic electroactive polymers (Bar-Cohen 154). Generally, a polymer's swelling potential increases as the number of cross links in its matrix decreases (Carpi, 19). A polymer with too few cross-links, though, will either fail to form or will be too weak upon formation and will fall apart during the application of compressive force (Uhlmann; Myata et al.)

By utilizing an antibody- complexed polymer gel network, Miyata et al. demonstrated the importance of cross-link density. Antibodies attached to the polymer network remained bound to each other until an antigen was released into the surrounding solution; the antibodies then detached from each other and attached to the antigen, causing cross-links to release and consequentially creating causing the polymer to swell (Myata et al). Myata et al., also demonstrated the importance of cross-link density in polymers and its relationship to

strength by demonstrating that the compressive modulus of the polymers decreased when there was less cross-link density in the polymers (i.e. when antigen was added) (Myata et al).

1.1.4.3. Crystallinity

A polymer's chains can be amorphous (exist in a completely random form with no order), they can be entirely crystalline (oriented in structure), or they can be anywhere in-between (semi-crystalline) (Uhlmann). A polymer's crystallinity depends on the chemichal makeup and the structure of the polymer chains; for example, a polymer with non-polar chains that are flexible naturally becomes extremely tangled and has little order (Gowariker, 178). One the other hand, polar polymers and polymers with large side-chains achieve high levels of crystallinity/order (Gowariker, 178).

A polymer's crystallinity has a great effect several properties: transparency, strength (modulus), permeability, heat capacity, density and stretching ability (Uhlmann; Gowariker, 189). A less-crystalline polymer is naturally less dense and weaker (lower modulus) (Gowariker, 190). In addition, studies have shown that a less-crystalline polymer will be more permeable to liquids and gasses, an important concept for ionic electroactive polymers because ions from the surrounding electrolyte solution must be able to penetrate the polymer's matrix in order for expansion of the polymer to occur (Gowariker, 191). Sadly, though, making ionic electroactive polymers completely amorphous (non-crystalline) should not be done because studies have shown that regions of polymers with little crystallinity degrade much easier than regions of polymers with high crystallinity (Gowariker, 192). In addition, an amorphous polymer will be more brittle than a crystalline polymer; the increase in polymer strength as crystallinity increases occurs because the crystalline sections of the polymer can slip when stress is applied, dispersing some of the force (Bar-Cohen 157).

In regards to transparency and heat capacity, a more crystalline polymer will diffract more light thus will be more opaque. A crystalline polymer will also be more resistant to heat (have a higher heat capacity). A polymer with a high degree of crystallinity will not however, be able to stretch as well as an amorphous polymer, although this may be in only one direction (Uhlmann). For example: tape can be pulled in one direction without breaking, while it tears in the opposite direction. A single-axis orientation is performed by physically pulling on a polymer in one direction (along one axis) while it is still hot (Uhlmann). Biaxial orientation (2-axis orientation) can also be performed in order to make more complicated shapes, such as a plastic soda bottle found in vending machines (Uhlmann).

1.1.5. Transport Properties of Ionic Electroactive Polymers

The transport properties of ions into and out of an ionic electroactive polymer's matrix are important because ion transport (and/or water transport) is responsible for the swelling abilities of ionic electroactive polymers. The simplest equation for passive diffusion is: $\frac{x^2}{2D}$ (Bar-Cohen 155). D is the diffusion coefficient, which will be very small (on the order of 10^{-6} cm^2/sec), and x is the distance that the water/ions need to travel (Bar-Cohen 155; Carpi, 15). The electroactive polymers tested in this report will be elaborated on later; however, it is important to note that due to their 3mm disk-like shape, the above equation indicates that, without any external factors speeding up or slowing down the diffusion time, about one hour's worth of diffusion throughout the entire polymer will result. Therefore, the distance that fluid must flow into a polymer (and, consequently, the size of the polymer) has a great effect of the polymer's swelling speed and ability; the larger the distance that fluid must flow (the larger the polymer), the longer it will take for a polymer to completely take up water (Bar-Cohen, 156).

There are other factors, though, that act to either speed up or slow down the ion/water transport into and out of ionic electroactive polymers. The first, most important factor is the amount of water in the polymer's matrix. As the polymer swells, the amount of water entering the polymer matrix over time tends to decrease as there is a maximum amount of water that the polymer can hold(Carpi, 15). Changes in temperature and pH can also slow down the flow of water/ions into the polymer's matrix; the polymer's density can increase due to an outflow of water from the gel by pressure gradients established by these changes (synresis), making it difficult for water to re-enter the polymer (Bar-Cohen, 155).

1.1.6. Electrochemistry and Electroactive Polymers

1.1.6.1. Oxidation/reduction, and what happens at the cathode/anode

As current is applied to an electroactive polymer submerged in an electrolyte fluid, the current from the electrode moves from the electrode to the electrolyte fluid, with electrons moving in the opposite direction (Webster, 183). At the same time, positively charged ions, cations (Na^+, for example), will travel in the same direction as the current through the electrolyte fluid; anions, negatively charged ions (Cl^-, for example), will travel in the opposite direction as the current (they travel in the same direction as the electrons) (Webster, 184). When the current in the system is flowing from the electrode toward the electrolyte, the oxidizing (electron-losing) reactions will be favored; this occurs at the anode in the cell. The reduction (electron-gaining) reactions are favored when the current proceeds from electrolyte to electrode; this occurs at the cathode (Webster, 184).

The distribution of ions very close to the electrode is a highly-studied area, with many different theories that exist to explain it (Webster, 185). Two formerly published papers have outlined the fact that ionic electroactive polymers placed in a space between two electrodes

(polyacrylic acid-type polymers, specifically) would bend away from the anode (Bar-Cohen, 159). (Remember that current around the anode flows from the electrode into the electrolyte solution, and therefore the oxidizing reactions are favored with the cations in the solution travelling away from the anode). Interestingly, the same experiment with the polymer touching the anode causes the polymer to bend in the opposite direction (Bar-Cohen, 159).

Diffusion is the simple reason that the ionic electroactive polymers bend in different directions depending on whether or not they are contacting the electrode or not (Bar-Cohen, 159). When the ionic electroactive polymer touches the anode, the acidic conditions surrounding the anode far overwhelm the conditions in the surrounding electrolyte solution causing the polymer to take on a large electric charge on one side and bend accordingly; when the polymer is not in contact with the electrode, the properties of the surrounding electrolyte fluid and its diffusion into the polymer take precedence in the system, and the polymer bends in the opposite direction (Bar-Cohen, 159).

1.1.6.2. pH change: the mechanism of actuation for electroactive polymers

Each electroactive polymer has a pH region of maximum swelling, depending on the polymer's chemical makeup (Bar-Cohen, 159). The standard electrode potential, E^0, which will be elaborated on later, can be used to measure the ease at which a substance becomes oxidized or reduced (Silberberg 908). During the application of an electric charge to the electrochemical cell housing the polymer and electrolyte solution, the voltage of the cell exceeds the standard electrode potential of the water, but does not exceed the standard electrode potential of the electrolyte solutions. The water is then split into oxygen and hydrogen, and the pH of the solution changes. This can be seen in the following table:

Table 1 List of Standard Electrode Potentials for Water. Reference electrode: 2 H+ + 2e− H2(g) (SHE)

Electrode	E^0 (Standard Electrode Potential, V)	Equation
Anode	0.82	$2\,H_2O(l) \rightarrow O_2(g) + 4\,H^+(aq) + 4e^-$
Cathode	−0.42	$2\,H_2O(l) + 2e^- \rightarrow H_2(g) + 2\,OH^-(aq)$

Information courtesy: Silberberg, page 932

The solution at the anode becomes acidic at a voltage above 0.82V, as water splits into hydrogen atoms and oxygen gas; at the cathode, electrons are donated to the reaction and hydrogen gas and hydroxide ions are produced. Being able to control the pH of the solution using the application of a voltage to a cell containing an electrolyte solution is a very important concept in this paper; as will be discussed in more detail later, Medipacs' polymer swells in an acidic environment and the base-swelling polymer swells in an alkaline environment.

1.1.7. Electroactive Polymer Degradation and Erosion

Degradation is the process by which polymer chains are cut from the polymer, and is virtually the reverse process to polymer formation/curing (Göpferich). All polymers degrade, regardless of type, although the mode and speed of degradation depends on each polymer's independent chemical makeup (Göpferich). Degradation is very important to polymers in general, but it is particularly important to ionic electroactive polymers because it weakens the electroactive polymers' strength and mechanical stability; strength and mechanical stability are important qualities for the electroactive polymers to retain over time as they are often used as actuators or transducers (Göpferich; Bar-Cohen, 162).

Polymer erosion (a different process than degradation) involves the direct removal of entire polymer monomers from the polymer chain (Göpferich). As with degradation, erosion is also varies in speed depending on each individual polymer's characteristics and chemical

make-up (Göpferich). Important mechanisms of both degradation and erosion include: hydrolysis, oxidation, stress cracking, swelling, plasticization, mineralization, dissolution, changes in crystallinity, and fatigue (Uhlmann, Göpferich).

1.1.7.1. Degradation via Hydrolysis

Likely the most important of all of the polymer degradation processes is hydrolysis (Uhlmann, Göpferich). Hydrolysis generally leads to a "cutting" of the polymer chains and a virtual reversal of the curing process (although the polymer will lose considerable strength long before complete degradation occurs) (Uhlmann). Hydrolysis can, however, lead to cross-linking in some cases as well (Uhlmann). Depending on the strength of the bonds between polymer's atoms, the valence number of the polymer's atoms and the space around the bonds between the polymer's atoms, the hydrogen and hydroxide ions can virtually "steal" atoms right off of the polymer backbone. Note that hydrolysis is catalyzed if the reaction system is not at a neutral pH and is in an acidic or basic environment (Uhlmann). Interestingly, a polymer that begins to degrade in any form will often cause a pH change local to the area of degradation because many polymers, particularly electroactive polymers, are made up of acidic or basic molecules linked together (Uhlmann, Göpferich).

Due to a strain on the chemical bonds between atoms in the polymer, increased mechanical stress can also speed up hydrolysis (Uhlmann, Göpferich). ("Stress" in the mechanical engineering field is a measure of force acting on a body per area, with the same units as pressure $\sigma = \frac{F}{A} = P$). A polymer that is also more hydrophilic, or "water-loving," will hydrolyze faster than a hydrophobic, or "water-avoiding," polymer; this is particularly important because a hydrophilic ionic electroactive polymer submerged in an electrolyte

naturally wants to uptake water and, in the process, will bring the electrolyte into its matrix (hydrophilicity, at least to an extent, is desirable in ionic electroactive polymers).

1.1.7.2. Erosion Changes the Polymer's Structure

As monomers within the polymer begin to pull away as their bonds to the polymer matrix are cleaved, many different things can happen. The monomers can pull off of the surface of the polymer and float into the solution or they can become trapped inside the polymer matrix because they are too large to escape the confines of the polymer matrix; either way, depending on the solution and the chemical properties of the monomer, the monomers have the possibility of re-forming into a polymer that is separate from the original and that has different properties than the original (Göpferich). In addition, the monomers can also re-form onto the original polymer matrix or the polymer matrix can form new bonds with itself utilizing the atoms that the monomers detached from (Göpferich). The re-formation of bonds (re-crystallization) can change many of the polymer's properties, particularly its optical and structural properties (strength, and so on).

1.2. Electrochemistry Overview

1.2.1. Expansion Properties of the Polymers used in this Report

1.2.1.1. Medipacs' Polymer

Medipacs' polymer consists of a tri-amine (NH_2), Jeffamine T-403, and a di-epoxide, poly (ethylene glycol) diglycidyl ether; both compounds are mixed with water to produce the final polymer matrix. The reaction between these molecules is presented below:

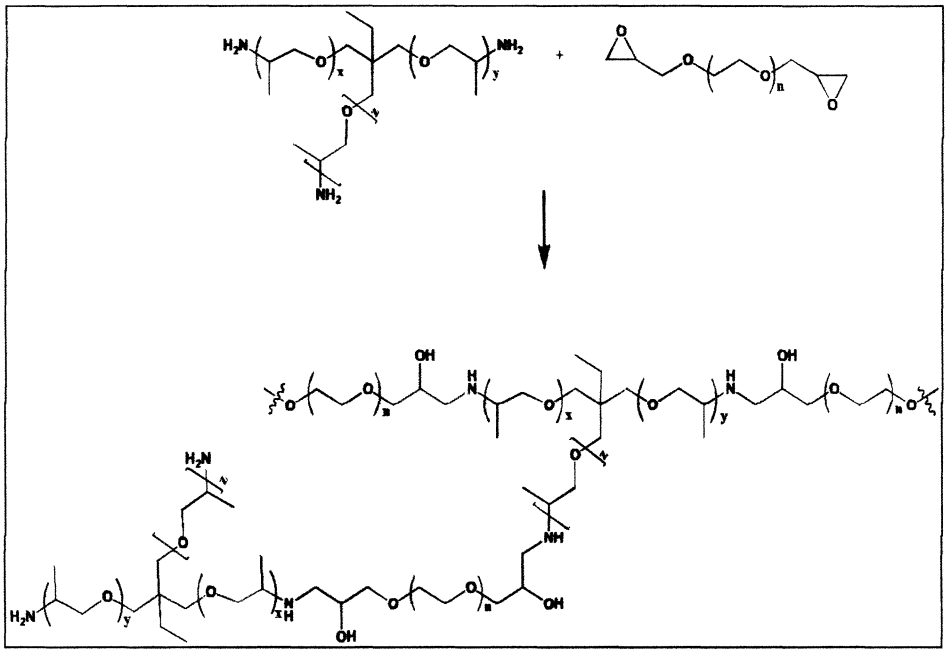

Figure 1 Formation of Medipacs' Polymer via Combination of Tri-Amine and Di-Epoxy

The polymer expands in a solution at a low pH when the amine (NH_2) groups take on a hydrogen atom (H^+) to form NH_3^+. The positive charges on the NH_3^+ molecules repel each other, and swelling occurs.

1.2.1.2. Base-Swelling Polymer

The base-swelling polymer used in this report consists of three different monomers (unlike Medipacs' polymer, which only has two): HEMA (2-hydroxyethyl methacrylate), AA (acrylic acid) and EGDMA (ethylene glycol-dimethacrylate). (Note that EGDMA is not the same as the poly (ethylene glycol) diglycidyl ether (polyEDGE) used in Medipacs' polymer). The chemicals used in the base-swelling polymer are shown below:

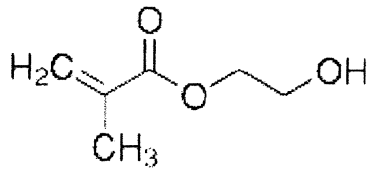

Figure 2 HEMA Monomer

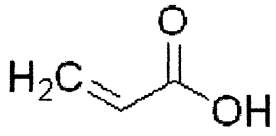

Figure 3 Acrylic Acid Monomer

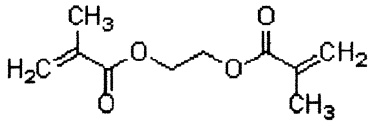

Figure 4 EGDMA Monomer

The base-swelling polymer's structure is illustrated below:

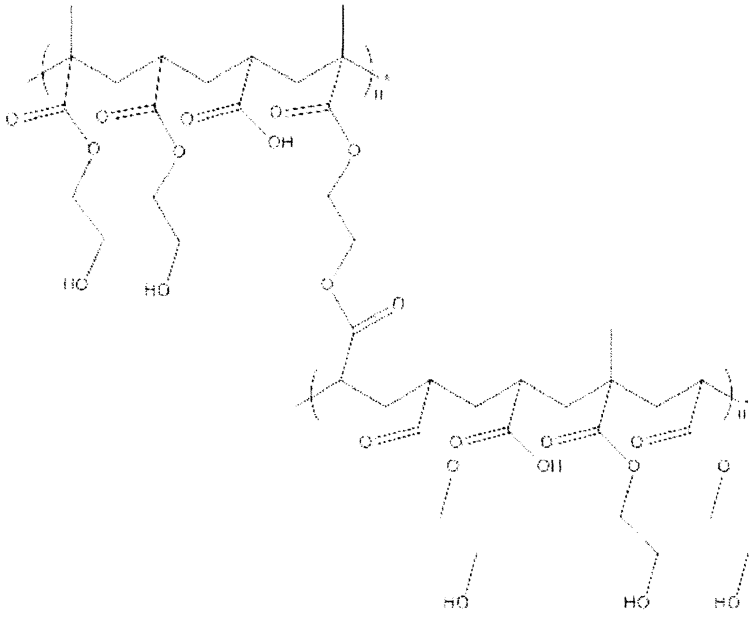

Figure 5 HEMA-AA Base-Swelling Polymer

Unlike Medipacs' polymer, the base-swelling polymer will expand when in contact with OH^- ions. The acrylic acid monomers (-COOH) present in the polymer structure facilitate swelling at high pH conditions in which the acid moieties are in their negatively charged carboxylate (RCO-) form. The negatively charged oxygen molecules repel each other, and swelling occurs. (This expansion is analogous to the positively charged $NH3^+$ molecules repelling each other in Medipacs'polymer).

1.2.2. Electrochemical Stability

1.2.2.1. Initial Medipacs Experiment Background

The initial question that brought about this report dealt with the need to acquire the maximum polymer expansion possible with the lowest use of power and with minimum gas production. Sodium perchlorate (NaClO4) was initially used by Medipacs to conduct electricity in the electrochemical cell used to swell the polymer; however, the expansion properties improved significantly when sodium bicarbonate (NaHCO3) was introduced as a replacement to sodium perchlorate. Testing different electrolyte solutions may provide some insight into the mechanism as well as possibly provide even greater expansion properties than sodium bicarbonate.

1.2.2.2. pka Value Discussion/Hypothesis

K_a is a value that describes the acidic strength of a chemical; the higher the K_a of a chemical, more hydronium (H_3O^+) ions exist in the solution, and the more acidic the solution (Silberberg 761). The more common form of K_a expression, though, is the pK_a, the $-\log(K_a)$. The pK_a can tell us two important qualities about the chemical at hand. First, the pK_a values directly correspond to the pH scale (they are logarithmic); second, a chemical with a pK_a of less than 1 will remain the same in the solution at all pH levels (H_3O^+, for example, has a pK_a of -1.7) (Silberberg 766).

A chemical that cannot donate a hydrogen ion (H^+) to the reaction does not have an acid dissociation constant. Such chemicals can instead be evaluated by breaking their molecules up and looking at the conjugate acid/base strength, according to the Bronsted-Lowry acid-base definition (Silberberg 770).

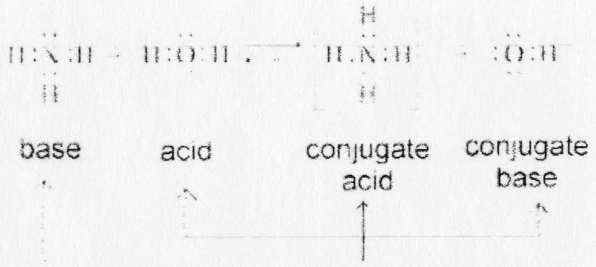

Figure 6 Illustration of conjugate acids and bases.
license-free at: http://www.saskschools.ca/curr_content/chem30_05/5_acids_bases/acids1_5.htm)

In water, which is considered a base, the reaction will tend to travel in a direction away from the stronger acid and stronger base, ending up with a weaker acid and weaker base in solution (Silberberg 770). Take one of the chemicals from this paper as an example: sodium perchlorate ($NaClO_4$). Sodium perchlorate can be broken up into the Na^+ and ClO_4^- constituents, with Na^+ bonding weakly with water in solution because it is the cation of a strong base (NaOH) (Silberberg, 787). The ClO_4^- ion, a weak conjugate base of a very strong acid ($HClO_4$), also tends to exist by itself in solution (Silberberg 771). As a general rule, stronger acids have weaker conjugate bases, and stronger bases have weaker conjugate acids.

Once again, looking at the acid/base and conjugate acid/conjugate base relationship is important when evaluating chemicals that don't have pK_a values and cannot donate a hydrogen atom, like sodium perchlorate. This same relationship applies to another chemical from this report, sodium nitrate ($NaNO_3$); the conjugate acid of sodium nitrate is nitric acid

(HNO_3). Due to the similarity between sodium perchlorate and sodium nitrate in acid/base reactions, it is expected that they perform similarly in the experiments in this report.

The pK_a values of the other three electrolytes from this report, sodium bicarbonate, sodium hydrogen sulfate, and citric acid are as follows:

Table 2 pKa Values of Solutions from this Report

Solution	pKa Value(s)
Sodium Bicarbonate ($NaHCO_3$)	10.3, 6.341 (carbonic acid)
Sodium Hydrogen Sulfate ($NaHSO_4$)	1.99
Citric Acid ($C_6H_8O_7$)	6.41, 4.75, 3.09

Values obtained from Wikipedia.com

The hypothesis for the experiments in this report looked at the acid-dissociation constants of sodium bicarbonate and asked two questions. First, does the acid dissociation constant play a critical role in swelling for Medipacs' polymer, and is that the reason that sodium bicarbonate outperformed sodium perchlorate in swelling; second, if the acid dissociation constant does play a role in Medipacs' polymer's swelling, will an electrolyte with multiple acid dissociation constants improve swelling even further? Citric acid was chosen to further test the hypothesis that multiple pK_a values will have a positive effect on Medipacs' polymer's swelling. Sodium hydrogen sulfate was chosen because it had a single hydrogen atom to donate to the reaction.

1.2.2.3. Oxidation/Reduction of the Electrolyte Solutions in this Report

An oxidation-reduction reaction involves the movement of electrons from one chemical to another; in addition, a clear understanding of oxidation-reduction reactions can also help explain the stability of electrolyte solutions during the application of an electric current, (Silberberg 893). The standard electrode potential, E^0, can be used to measure the ease at

which a substance becomes oxidized or reduced; the more positive the standard electrode potential, the more readily the reaction occurs (Silberberg 908). Two charts of ions pertaining to the electrolytes and experiments in this paper are listed below; as is the convention, all reactions are written as reductions:

Table 3 List of Standard Electrode Potentials for Electrolyte Solutions from this Report. Reference electrode: 2H+ + 2e– H2(g)

Ion	E^0 (Standard Electrode Potential, V)	Balanced Half-Reaction
$SO4.^{2-}$	2.01[#]	$S_2O_8^{2-}(aq) + 2e^- \leftrightarrow 2SO_4^{2-}(aq)$
$C_6H_5O_7^-$	1.2*	N/A
$ClO4^-$	1.2	$ClO_4^- + 2H^+ + 2e^- \leftrightarrow ClO_3^- + H_2O$
$NO3^-$	0.80	$NO_3^-(aq) + 2H^+ + e^- \leftrightarrow NO_2(g) + H_2O$
H_2O	0.82	$O_2(g) + 4\ H^+(aq) + 4e^- \leftrightarrow 2\ H2O(l)$
$HCO3^-$	-	CO2 participates in the reaction instead[1]
H+ Std.	0.00	$2H^+ + 2e^- \leftrightarrow H_2(g)$
CO_2	-0.11	$CO_2(g) + 2H^+ + 2e^- \leftrightarrow HCOOH(aq)$
H_2O	-0.42	$2\,H2O + 2e- \leftrightarrow H2(g) + 2OH-$
$Al3^+$	-1.66	$Al^{3+} + 3e \leftrightarrow Al^o$
Na^+	-2.71	$Na^+ + e \leftrightarrow Na^o$

Information obtained from Wikipedia.com, except: ([1]) Osetrova et al, (*) Gonzalez-Pena et al, and ([#]) knowledgerush.com

Table 4 List of Standard Electrode Potentials from Table 3 Corrected for their Concentrations from this paper using the Nernst Equation

Ion	E0 Adjusted to 0.02M	E0 Adjusted to 0.06M	E0 Adjusted to 0.1M
$SO4.^{2-}$	2.17	2.14	2.13
$C_6H_5O_7^-$	1.67	1.60	1.57
$ClO4^-$	1.43	1.25	1.39
$NO3^-$	1.03	1.00	0.99
H_2O	N/A	N/A	N/A
$HCO3^-$	-	-	-
H+ Std.	0.23	0.20	0.19

CO_2	0.12	0.09	0.08
H_2O	N/A	N/A	N/A
$Al3^+$	-1.50	-1.53	-1.54
Na^+	-2.24	-2.31	-2.34

Information obtained from Wikipedia.com, except: ([1]) Osetrova et al, (*) Gonzalez-Pena et al, and ([#]) knowledgerush.com

Sodium (Na^+) ions will dissociate when the electrolyte is dissolved in water (this concept applies for every electrolyte in this paper but citric acid); one example of this is sodium perchlorate: $NaClO_4 \leftrightarrow Na^+ + ClO_4^-$ in water. We also know that the citric acid, as it naturally exists in solution at a low pH, suffers the loss of one, two, or three of its hydrogen ions depending on the pH of the solution; the citrate ion, $C_6H_5O_7^{-3}$ in the table, is the de-protonated version of citric acid.

The ions in the tables above are sorted, from top to bottom, highest standard electrode potential to lowest standard electrode potential. (The above numbers also assume a constant temperature) (Silberberg, 915). The reaction listed next to the chemicals will occur if the voltage of the electrochemical cell exceeds the standard electrode potential. As mentioned in chapter 1.1.6.2., pH changes of the system directly affect the swelling abilities of electroactive polymers, including the two electroactive polymers in this report, Medipacs' polymer and the base-swelling polymer; pH changes of the system occur partly due to the splitting of water during the application of a voltage (otherwise known as electrolysis). When applying a voltage to the system, the voltage should not cause the electrolytes themselves to undergo a chemical reaction, but it should be enough to split water molecules--this can be done by applying a voltage above water's standard electrode potential, but below the standard electrode potential of the electrolytes. The standard electrode potentials from Table

3 list the standard electrode potentials at standard conditions, which are at a 1M concentration; therefore, Table 4 was constructed to show the adjusted standard electrode potentials under concentrations investigated in this report.

1.2.3. Effects of the Solvent: Osmotic Pressure, Conductivity, and so on

There are also other factors responsible for the polymer's performance in electrolyte solutions: the conductivity of the electrolyte is one of them. A highly conductive electrolyte will allow the electrochemical potential to reach farther in the polymer's expansion cell (Carpi, 207). Some electroactive polymers will employ different electrolytes, therefore, because they all require differing conductivities.

A second property of the electrolyte solutions is the ability of the solvent to move in-between the polymer chains and push them apart (Carpi, 207); this is important because electroactive polymer chains that are coiled up or tangled up shield their functional groups from ions that induce expansion. An electrolyte solution that can get in-between the polymer chains can open up the chains and allow for faster ion diffusion into the polymer's matrix; this will help to speed up the actuation of the polymer.

Finally, osmotic pressure can develop when ions diffuse into and out of the polymer's matrix (Carpi, 207). This is particularly important because a polymer submerged in an electrolyte with a low ion concentration can cause the solvent in the solution to diffuse into the polymer due to osmotic pressure as a way of evening out the concentration gradient; if the ion concentration inside the polymer decreases, the solvent drains out of the polymer and shrinkage occurs instead (Carpi, 207). Keep in mind—this osmotic effect occurs due to osmotic pressure from the electrolyte, but the solvent does the diffusing.

2. Materials and Methods

A flow chart is included in the appendix that outlines the materials and methods section.

2.1. Medipacs' Polymer Formation

Polyethylene glycol diglycidyl ether was purchased from Sigma Aldrich, and JEFFAMINE® T-403 was donated by the Huntsman Chemical Company; both chemicals were used as received. Unless otherwise stated, DI water was used for all experiments in this report.

A 50mL beaker was placed on an Ohaus Adventurer™ balance and zeroed. Then, 2.886g JEFFAMINE® T-403 was weighed out using a glass pipette followed by 3.881g polyethylene glycol diglycidyl ether before the JEFFAMINE® T-403 and polyethylene glycol diglycidyl ether were mixed for 10 minutes on top of a hot plate using a 1/2" by 5/16" Teflon® magnetic stir bar. Following the stirring, the beaker was again zeroed on the Ohaus Adventurer™ balance and 6.767g DI water was placed into the mixture using a glass pipette. The new mixture was then stirred on a hot plate for 15 minutes (also using a 1/2-inch by 5/16-inch Teflon® magnetic stir bar).

Next, the reaction mixture was placed into a 2.5-inch in diameter (1 inch deep) stainless steel cupcake tray mold and was heated in an oven at 60°C for 5 hours. After heating, the polymers were allowed to cool to room temperature (24°C±1°) for 19 hours before being peeled out of the mold.

2.2. Initial Studies

Two initial studies were carried out on various electrolyte solutions to evaluate their effect on the Medipacs' polymer in both active and passive swelling forms. These

experiments were performed prior to the study that is main the subject of this report; however, their results are the basis for the research that this report is based on.

2.2.1. Sodium Bicarbonate/Sodium Perchlorate Passive Swelling

A 200mL plastic polyethylene tub (1.3 inches deep and 3.5 inches in diameter) was placed on an Ohaus Adventurer™ balance and zeroed. Dry, pre-made Medipacs' polymer (1 day old) was cut into 1-inch long by 1/2-inch wide by 1/8-inch thick segments with scissors and 5 grams of segments was weighed out into the zeroed tub. Then, a 1/4-inch hole-puncher was used to produce five cylinder-shaped polymer pieces from the same polymer; the polymer pieces were weighed as a whole and were then placed into the tub along with the polymer pieces cut out with scissors. 150mL of the electrolyte being tested was placed into the tub using a 250mL graduated cylinder (with markings every 1mL), and the initial pH of the solution was measured. Then, a lid was placed on the tub to seal it and prevent evaporation. Two tubs were made for each solution to provide two sets of data for each electrolyte being tested. The polymer cylinders were then weighed at 2, 4, 24, and 48 hours; the pH of the solutions was also measured at 2, 4, 24, and 48 hours. The hydration percentage (amount of water that the polymers had taken up) was calculated for each weight measurement using the following equation: $\frac{Weight\ After\ Hydrating - Weight\ Before\ Hydrating}{Weight\ Before\ Hydrating} * 100\% = Hydration\ Percent.$

2.2.2. Sodium Bicarbonate/Sodium Perchlorate Active Swelling

Some of the fine details of the processing of Medipacs' polymer for the active swelling experiments are proprietary and beyond the scope of this report. After processing, a set amount of pre-made Medipacs' polymer was placed inside a 200mL plastic polyethylene tub (see chapter 2.2.1) and 150mL of a 0.05M concentration electrolyte (sodium bicarbonate or

sodium perchlorate) was placed inside the tub. The polymer was then allowed to hydrate (take up water) while sitting still inside the tub for a period of 24 hours.

2.2.2.1. Setup

After the 24 hour hydration period, the Medipacs' polymer was processed further before being placed onto an aluminum electrode sitting flush on the bottom of a ~1.5 inch diameter porous bowl (Celgard). A 1.06-inch diameter cylindrical weight was placed onto the polymer (but not touching the sides of the bowl) to simulate internal infusion pump pressure (a target of 0.78 PSI pressure was used to determine the 396g weight of the cylinder). Then, the porous bowl, polymers, and weight were placed into a 200mL plastic polyethylene tub identical to the tub used to hydrate the polymers; no lid was placed on the tub. A second platinum electrode was cut out and placed around the perimeter of the porous bowl (the shape of the electrode resembled a cylinder with no top or bottom).

2.2.2.2. Active Swelling Measurement

A low-intensity 670nm laser was then placed about one inch from the top of the cylindrical weight and was secured to point straight down onto the top face of the cylindrical weight. As the difference in height from the cylindrical weight to the laser was used to measure the vertical expansion of the polymers, data from the laser was continually sampled via a (proprietary) LabView program for every tenth of a second for a period of at least 30 minutes. The final height of the polymer was determined from the results, and the results from each of the electrolyte solutions were compared.

2.3. Medipacs' Polymer Passive Swelling

Initially, the experiments for this report (passive and active swelling) set out to study the correspondence of the pK_a value of different electrolytes and the electrolytes' effect on polymer performance based on their differing pka values. The theory behind the proposal

relied on previous knowledge that the Medipacs Polymer would swell in an acidic solution, and that the added electrolyte's pka value determines the pH value at which the electrolyte will begin to dissociate into its different chemical constituents (as discussed before, $HA \leftrightarrow A^- + H^+$).

2.3.1. Medipacs' Polymer Passive Swelling Procedure (Initial)

2.3.1.1. Preparation of Polymer/Solutions

The pre-made Medipacs polymer (see chapter 2.1 for Medipacs' polymer formation steps) was cut into 1/8"-diameter cylinders using a hole-puncher to achieve a uniform shape throughout the course of the experiments. Citric acid ($C_6H_8O_7$), sodium bicarbonate ($NaHCO_3$) and sodium perchlorate ($NaClO_4$) electrolyte solutions were purchased from Sigma Aldrich; all chemicals were used as received.

For each electrolyte solution, a weigh-boat was placed onto an Ohaus Adventurer™ balance and the balance was zeroed. The proper amount of each electrolyte was weighed out onto the weigh boat to yield the proper molarity in solution (0.02M, 0.06M., or 0.1M); in the meantime, 500mL of DI water (measured in a 500mL graduated cylinder) was poured into a 1L glass beaker, which was in turn placed onto a hot plate for stirring. The weighed out chemical in the weigh boat was then emptied into the 1L beaker, and another 500mL from a graduated cylinder was used to wash electrolyte stuck to the weigh boat into the beaker. Using a 5/16-inch by 1-inch Teflon® stir bar, the solution was stirred for 30 minutes before being emptied into a 1-liter, clear glass bottle via a glass funnel. Each electrolyte solution was made in a concentration of 0.02M, 0.06M, and 0.1M using the equation:

$$Liters\ of\ Solution * Molecular\ Weight\ of\ Electrolyte * Target\ Molarity = Grams\ of\ Chemical\ to\ Add.$$

2.3.1.2. Passive Swelling Procedure

In order to simulate an active swelling environment during passive swelling, the pH of each of the polymer electrolyte solutions was adjusted using hydrochloric acid (HCl) to lower the pH and by using sodium hydroxide (NaOH) to raise the pH. Hydrochloric acid solution was purchased from Sigma Aldrich and was used as received; sodium hydroxide pellets were also purchased from Sigma Aldrich, and 120 grams of sodium hydroxide pellets were mixed with 250 mL DI water to make 12M sodium hydroxide solution for use in the experiments.

In order to adjust the pH of each electrolyte solution to a range of integers from 1 to 10, a 50mL beaker with a 5/16-inch by 1/2-inch stir bar was placed on a hot plate, and then 25mL of the target solution was placed into the beaker. In order to hold the pH meter's electrode above the spinning stir bar and prevent damage, a ring stand was placed above the beaker and the electrode was threaded through the hole in the stand. In order to uphold good laboratory practices (GLP), the pH meter used was also calibrated before each use using buffer solutions of pH 4, 7 and 10 (the meter's linear range was calibrated depending on the pH being measured); in addition, the pH meter was re-calibrated every 2 hours during its use.

When adjusting the pH, two separate 1mL Sub-Q (26G5/8) PrecisionGlide needles were used: one for sodium hydroxide and one for hydrochloric acid. When the pH of the solution reached the desired pH, the pH was recorded and the solution was placed into a 50mL vial. Then, 3 pre-cut-out Medipacs' polymer cylinders were weighed together on an Ohaus Adventurer™ balance and an initial dry weight for the polymers was recorded before the polymers were placed into the 50mL vial. The 50mL vial was then sealed, and the polymers were left to sit in the solution.

The pH of the solutions was checked at 24 hours and at 1 week (168 hours). While checking the pH of the solutions, the polymers were removed from the solution using a small metal spatula and blotted dry on a paper towel; special attention was given to make sure that the solution was only dried from the outer surface of the polymers by making quick measurements and not allowing the polymers sufficient time to dry out, losing weight (and, consequentially, electrolyte solution that had been taken up).

2.3.2. Updated Medipacs' Polymer Passive Swelling Procedure

After an initial passive swelling experiment, a second passive swelling experiment was performed because weighing three polymer pieces as one did not give enough data points. Therefore, the passive swelling experiments were repeated as follows.

Preparation of Medipacs' polymer was identical to the procedure listed in chapter 2.3.1.1. In addition, the same sodium bicarbonate, citric acid and sodium perchlorate chemicals from 2.3.1.1. were used, although new solutions were made. (Note: new solutions were made and new polymers were made for each experiment in the report). A few procedural changes were incorporated for the updated experiments; these procedural changes are listed below.

First, while adjusting the pH of the solutions, the amount (and concentration) of sodium hydroxide and hydrochloric acid being added to the electrolyte solutions was measured. Second, after adjusting the pH of each electrolyte solution, the solution was split up and placed equally into 3 50mL vials. Then, each pre-made Medipacs' polymer piece was weighed was weighed individually (rather than 3 at a time) and each individual piece was placed into its own vial. Measurements from the vials were taken using the same steps as in chapter 2.3.1.2.

2.4. Base-Swelling Polymer Formation

2.4.1. First Attempt at Base-Swelling Polymer Formation

The base-swelling polymer is, like Medipacs' polymer, an ionic electroactive polymer. The polymer consists of 2-hydroxyethyl methacrylate (HEMA) monomer, acrylic acid (AA) monomer, ethyleneglycol-dimethacrylate (EGDMA) cross-linker, and 2,2-dimethoxy-2-phenyl-acetophenone (DMPA) photoinitiator. All products were purchased from Sigma Aldrich. The EGDMA and HEMA both contained an inhibitor, so they were filtered using 58 angstrom basic aluminum oxide from Alfa Aesar before being used. Although it did not contain an inhibitor, the acrylic acid (AA) was also filtered; however, the acrylic acid was filtered using 58 angstrom neutral aluminum oxide from Alfa Aesar. The DMPA was used as received.

The initial attempt at making the base-swelling polymer involved taking a 25mL glass vial and zeroing it on a balance. The pre-filtered chemicals (HEMA, AA, and EGDMA) were then weighed into the beaker using a pipette. The weight for each chemical and the order of addition for each chemical was: 2.064g HEMA, 0.0245g EGDMA, 0.27g AA. After adding the liquid chemicals, a rubber cap was placed on the vial and the reaction mixture was slowly bubbled for 15 minutes with argon gas to purge the atmosphere of oxygen.

After bubbling, 0.0737g DMPA was added using a small spatula. When adding the DMPA care was taken to minimize exposure to light because DMPA is a UV light-activated chemical. After the DMPA was added, the vial was completely covered with aluminum foil. The reaction mixture was then sonicated for 15 minutes. While sonicating, the outer surface of a 50mL beaker served as a template to make an aluminum foil mold for the reaction mixture; once the reaction mixture finished sonicating, it was poured into the aluminum foil

mold and then immediately placed into a UV reactor with a UV lamp located 2 inches above the reaction mixture where it cured for 1 hour. After curing, the aluminum foil was slowly peeled off of the polymer.

2.4.2. Base-Swelling Polymer "Side-by-Side" Experiments

A series of experiments was performed partly to improve the properties of the base-swelling polymer, but also because the initial formation did not fully cure.

2.4.2.1. Argon Gas Bubbling

One experiment was performed without argon gas bubbling and it was compared to a polymer made simultaneously with argon gas purging. Ultimately, it was determined that argon gas did not need to be used for future formulations.

2.4.2.2. AIBN

The thermal initiator, AIBN, was used as a substitute for DMPA to see if the resulting polymer would have properties desirable for the experiment at hand. Ultimately, AIBN, although it worked, was not used for polymer curing, although it was successful at polymer curing.

2.4.2.3. Beaker UV Curing

The polymer was placed directly into a beaker (rather than in an aluminum foil mold) and two polymer curing experiments were run. First, the beaker was placed directly onto the UV lamp inside the reactor so that the UV rays would shine through the bottom of the beaker. Secondly, the UV lamp was placed over the beaker and the UV rays were allowed to shine down on top of the reaction mixture. The UV lamp above the beaker was determined as the final polymer curing mechanism.

2.4.2.4. Teflon® mold

A Teflon® mold with a 0.1-inch deep "T"-shaped cut-out (0.5-inch-wide channels) was used as a template for curing a polymer; the UV lamp was placed above the polymer. In the end, the Teflon® mold did not work, and was therefore not used in polymer curing.

2.4.2.5. EGDMA/HEMA Ratio Change

The ratio of EGDMA to HEMA was altered by keeping the HEMA, AA, and DMPA amounts constant and varying the amount of EGDMA present in the reaction mixture; numerous experiments were performed with EGDMA concentrations consisting of: 5.8%, 6.2%, 9.4% and 12%. 9.4% EGDMA was used in the final base-swelling polymer formula.

2.5. Base-Swelling Polymer Passive Swelling

2.5.1. Pilot Study for New Passive Swelling Procedure

After the base-swelling polymer was formed, a study to limit the pH-change of the polymer's electrolyte solution was proposed; however, in order to check the feasibility of the study a pilot study was performed. In the pilot study, three different bottles of 0.1M sodium perchlorate solutions (250mL, 500mL, 1L) were adjusted to a pH of 8 with sodium hydroxide were created. Then, 3 pre-made base-swelling polymers were placed in each bottle. The pH of the bottles was checked and recorded after 24, 48, and 72 hours, and it was determined that the pH of the solution would not change in a 1L bottle for 72 hours of polymer swelling.

2.5.2. Base-Swelling Polymer Passive Swelling Experiments

The base-swelling polymer passive swelling procedure was identical to the chapter 2.3.2. procedure for the passive swelling of Medipacs' polymer; however, there were a few key differences. First, 1L bottles were used and 1L of solution was used. Secondly, thr3ee polymers were placed into the same bottle, while red and black permanent markers were used to color 2 of the 3 polymer pieces; this allowed the three polymer pieces in the same bottle to

be distinguished apart from each other (the third piece was left colorless). Finally, the 3 polymer pieces were individually weighed and the pH of each solution was taken after 24, 48, and 72 hours (in the previous experiment, the polymers were weighed and the pH was taken at 24 hours and at 168 hours).

2.6. Active Swelling Experiments

The same active swelling procedure was used for both the base-swelling polymer and Medipacs' polymer. A 1/4"-diameter circle was cut out of a pre-made polymer using a hole puncher, then a 1/8"-diameter circle was cut out of the center of the polymer punch-out to form a donut-like shape. The center of the polymer was punched-out to avoid the greater swelling that has been proven to happen in the center of the polymer in past experiments. The polymer was then placed into 100mL of DI water for a period of 24 hours to hydrate.

After hydrating, the polymer piece was placed into a Cel-Guard cup (approximately 1/2" inner diameter, and 1/4" tall). The Cel-Guard cup and polymer were then placed into a 200mL plastic weigh-boat, and two aluminum electrodes were placed in the setup. One of the aluminum electrodes formed a cylindrical shape and encircled the outside of the Cel-Guard cup; the second aluminum electrode formed a circular shape (with an approximately ½" diameter) and was placed directly on top of the polymer in the setup. Finally, a weight was placed on top of the inner electrode (263g for Medipacs' polymer and 22.01g for the base-swelling polymer).

The setup was then placed under an OPTOncdt low-power 670nm laser, and 50mL of the target electrolyte was poured over the Cel-Guard setup. The electrodes (anode on inside of Cel-Guard material and cathode on outside of Cel-Guard material for Medipacs' polymer) were then attached to a power supply controlled by a LabVIEW program.. The LabVIEW

program was set up to keep a constant current in the system of 10mA and measure the distance between the system and the laser every three seconds in order to determine the amount that the polymer actuator expanded. Finally, the system was started and allowed to run for 1800 seconds (30 minutes) before automatically shutting off. Immediately after the active-swelling period ended, the polymer was weighed and the pH of the inner portion of the Cel-Guard material was taken and recorded (this information is not present in this report, but is present in supplementary materials). For the base-swelling polymer, the electrodes were reversed so that the cathode was placed on the inside of the Cel-Guard cup and the anode was placed on the outside of the Cel-Guard cup.

3. Results

3.1. Initial Studies

The results from the initial studies that are the basis for this report have been included in section 3.1.

3.1.1. Sodium Bicarbonate/Sodium Perchlorate Passive Swelling

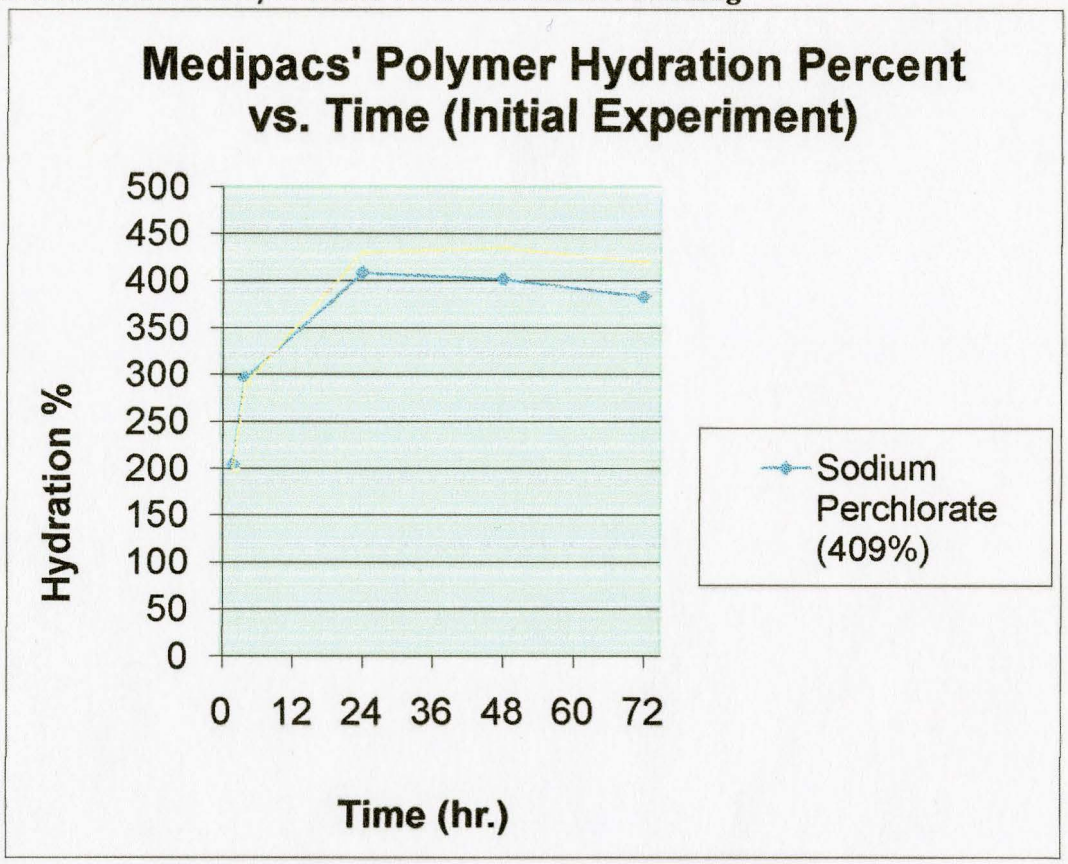

Figure 7 Initial Sodium Bicarbonate/Sodium Perchlorate Passive Swelling Experiment Results

Notice that in Figure 7 the swelling reaches a peak at around 24 hours before it begins to slowly decline. Previous experiments by Dr. Dominique McGrath (University of Arizona) and Dr. Pallavi Rao (University of Arizona) have shown that Medipacs' polymer actually continues to swell for up to three months before it stops taking on electrolyte; however, after 24 hours the polymer's swelling has virtually asymptoted, and the polymer will swell very slowly afterward.

3.1.2. Sodium Bicarbonate/Sodium Perchlorate Active Swelling

The active swelling results showed a much larger difference in performance between sodium perchlorate and sodium bicarbonate than the passive swelling results, with sodium

bicarbonate showing an increase in performance six times greater than sodium perchlorate (1.2mm stroke distance versus 0.18mm stroke distance) during one half hour of continuous 10mA current.

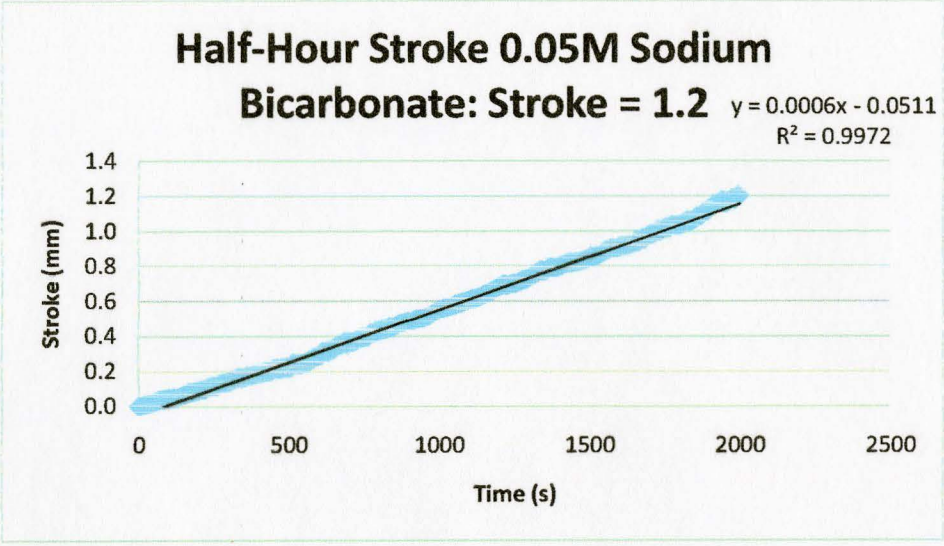

Figure 8 Initial Sodium Bicarbonate Active Swelling Experiment Results

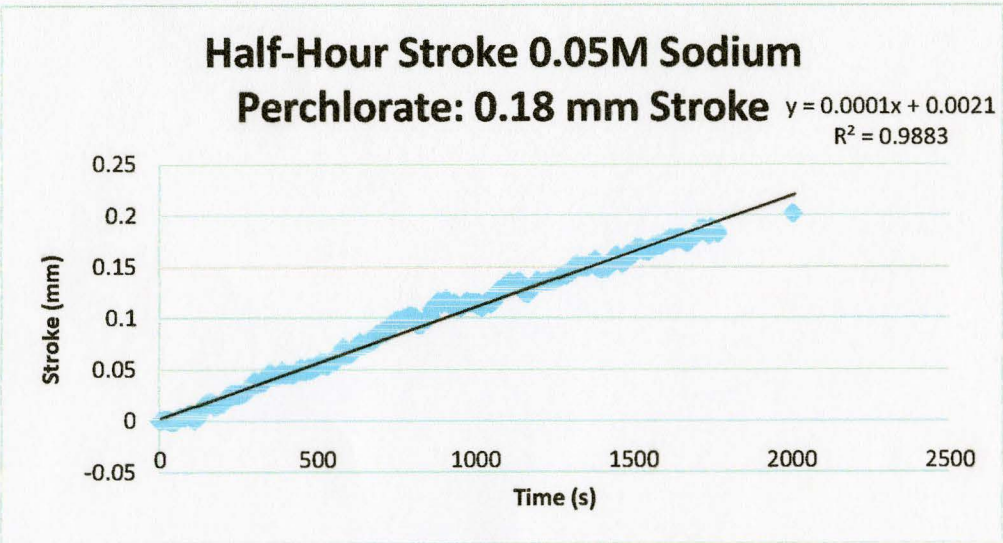

Figure 9 Initial Sodium Bicarbonate Active Swelling Experiment Results

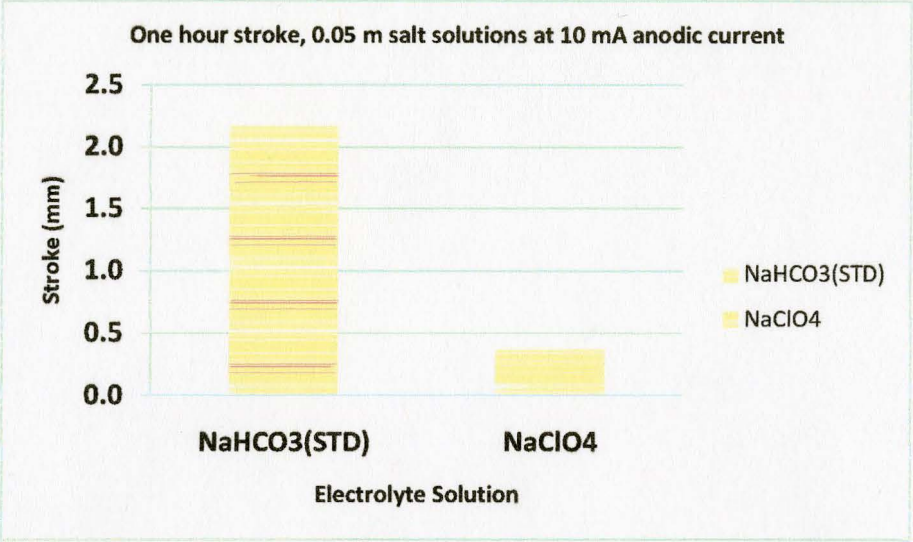

Figure 10 Comparison of Initial Sodium Bicarbonate and Sodium Perchlorate Active Swelling Results

3.2. Medipacs' Polymer Passive Swelling

3.2.1. Medipacs' Polymer Passive Swelling Procedure

3.2.1.1. Effect of Electrolyte Concentration on Hydration

The different electrolyte solutions were individually evaluated for their polymer swelling abilities based on a change in their concentration levels. Each concentration level was compared to the concentration level below it and evaluated for its significance via an unpaired student's t-test (for example, a 0.06M electrolyte was compared to a 0.02M electrolyte). To measure the 0.02M electrolyte concentration's effect on the swelling abilities of the polymer, a DI water control (no electrolyte) was used. A table listing the p-values (with a 95% confidence) was placed after each graph. The t-test was conducted using Microsoft Excel's built-in t-test calculator (function: TTEST=(array1,array2,tails,type), where "type" means unpaired or paired).

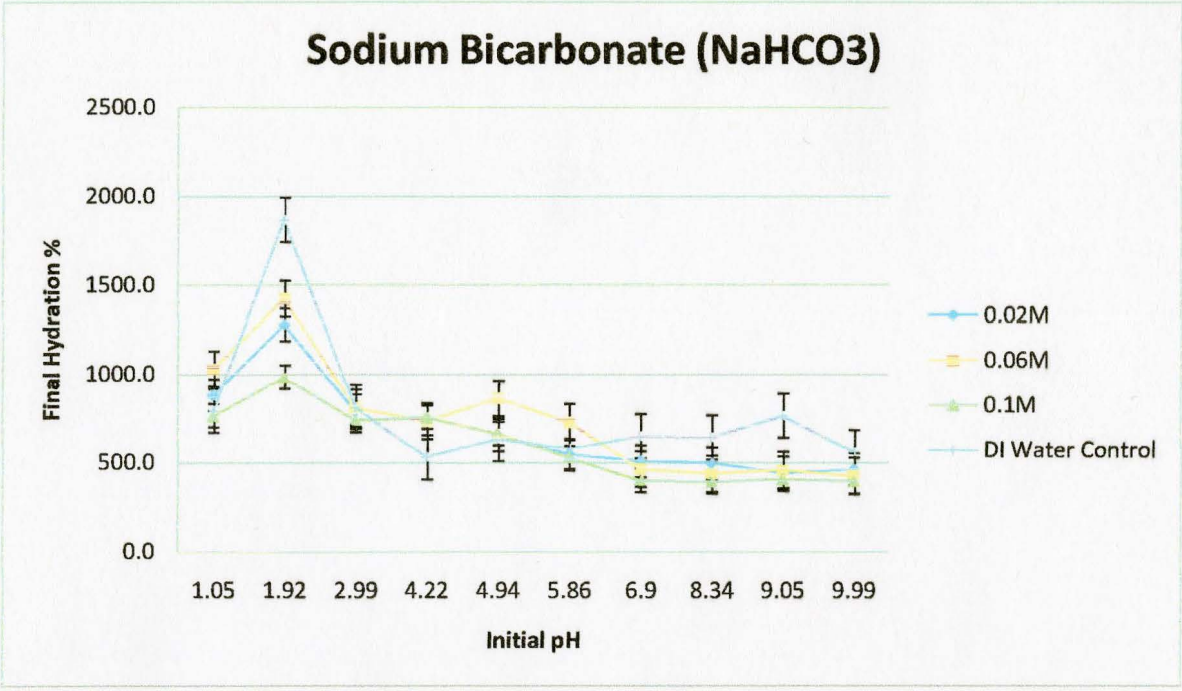

Figure 11 Sodium Bicarbonate Passive Swelling - Comparison of Differing Electrolyte Concentrations

Table 5 Sodium Bicarbonate t-test Results: Comparison of Differing Electrolyte Concentrations

NaHCO3 T-Test Results	DI Water vs. 0.02M	0.02M vs. 0.06M	0.06M vs. 0.1M
P-Value	0.028	0.174	0.008
Significant? (95% Confidence)	Yes	No	Yes

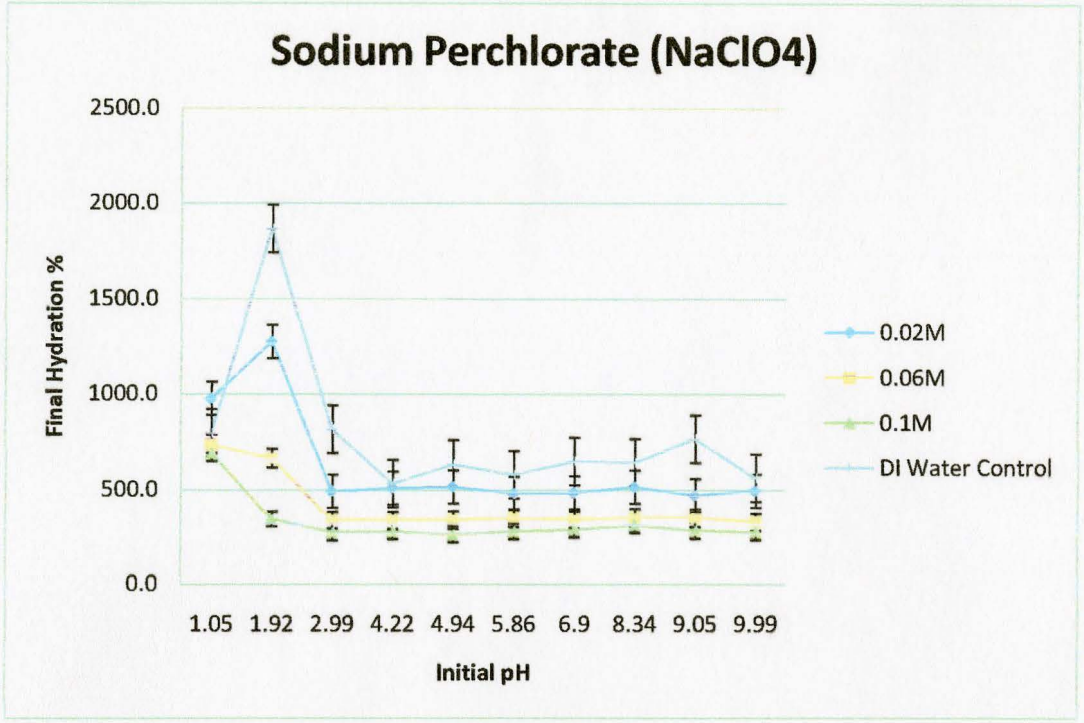

Figure 12 Sodium Perchlorate Passive Swelling - Comparison of Differing Electrolyte Concentrations

Table 6 Sodium Perchlorate t-test Results: Comparison of Differing Electrolyte Concentrations

NaClO4 T-Test Results	DI Water vs. 0.02M	0.02M vs. 0.06M	0.06M vs. 0.1M
P-Value	0.001	0.000	0.000
Significant? (95% Confidence)	Yes	Yes	Yes

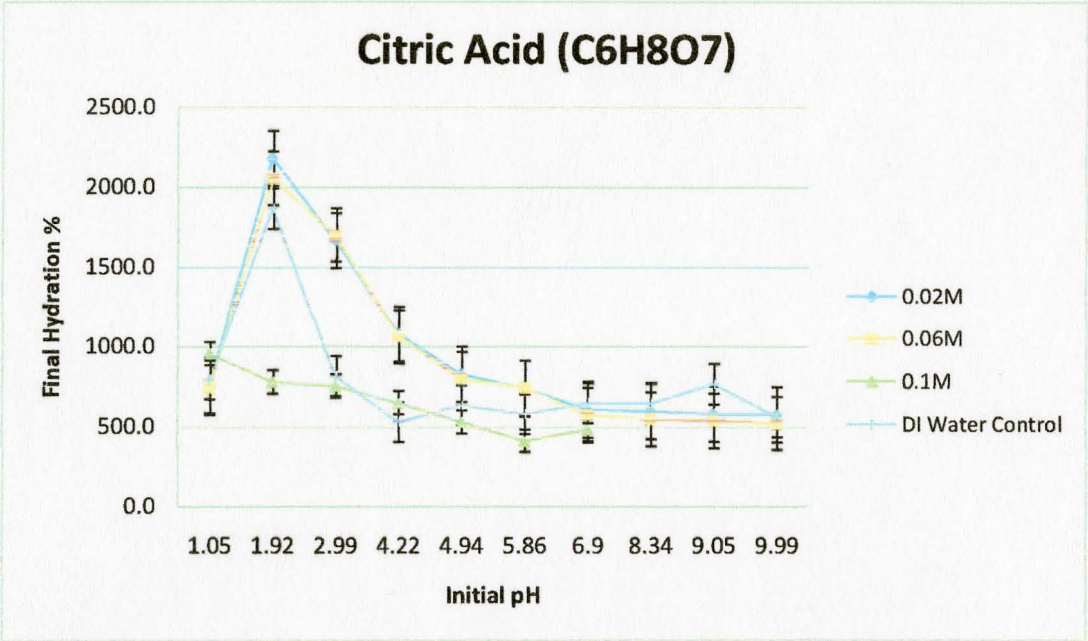

Figure 13 Citric Acid Passive Swelling - Comparison of Differing Electrolyte Concentrations

Table 7 Citric Acid t-test Results: Comparison of Differing Electrolyte Concentrations

Citric Acid T-Test Results	DI Water vs. 0.02M	0.02M vs. 0.06M	0.06M vs. 0.1M
P-Value	0.005	0.188	0.019
Significant? (95% Confidence)	Yes	No	Yes

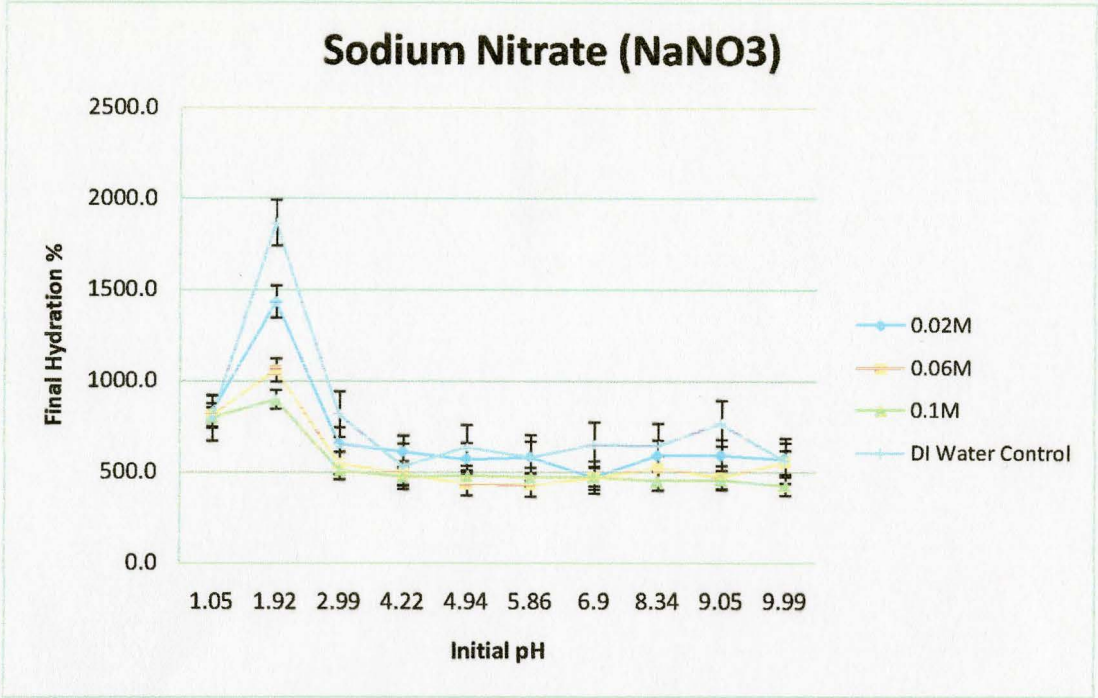

Figure 14 Sodium Nitrate Passive Swelling - Comparison of Differing Electrolyte Concentrations

Table 8 Sodium Nitrate t-test Results: Comparison of Differing Electrolyte Concentrations

NaNO3 T-Test Results	DI Water vs. 0.02M	0.02M vs. 0.06M	0.06M vs. 0.1M
P-Value	0.006	0.000	0.026
Significant? (95% Confidence)	Yes	Yes	Yes

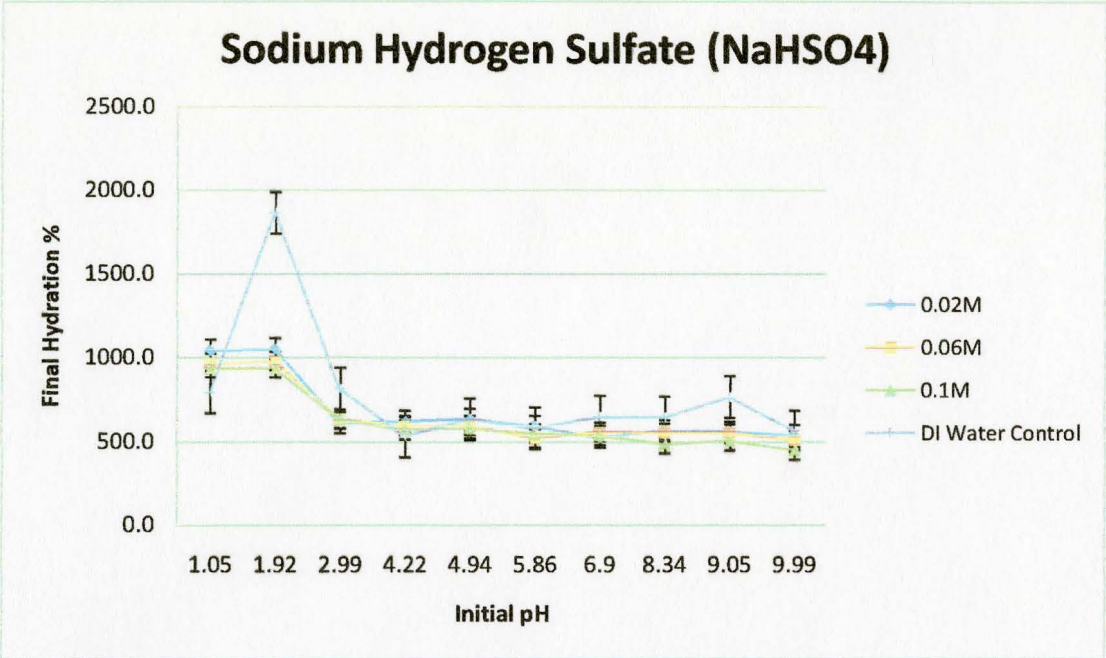

Figure 15 Sodium Hydrogen Sulfate Passive Swelling - Comparison of Differing Electrolyte Concentrations

Table 9 Sodium Hydrogen Sulfate t-test Results: Comparison of Differing Electrolyte Concentrations

NaHSO4 T-Test Results	DI Water vs. 0.02M	0.02M vs. 0.06M	0.06M vs. 0.1M
P-Value	0.047	0.030	0.005
Significant? (95% Confidence)	Yes	Yes	Yes

3.2.1.2. Comparison of the Hydration Abilities of Different Electrolytes

A comparison of each electrolyte was made relative to sodium perchlorate (the original electrolyte) at each concentration. For example, all electrolytes were compared to sodium perchlorate at a concentration of 0.02M, and then a separate comparison was performed at 0.06M (and so on). The same Excel t-test as in Chapter 3.2.1.1 (above) was run for each comparison. (As a reminder, the t-test is an unpaired, 2-tail t-test).

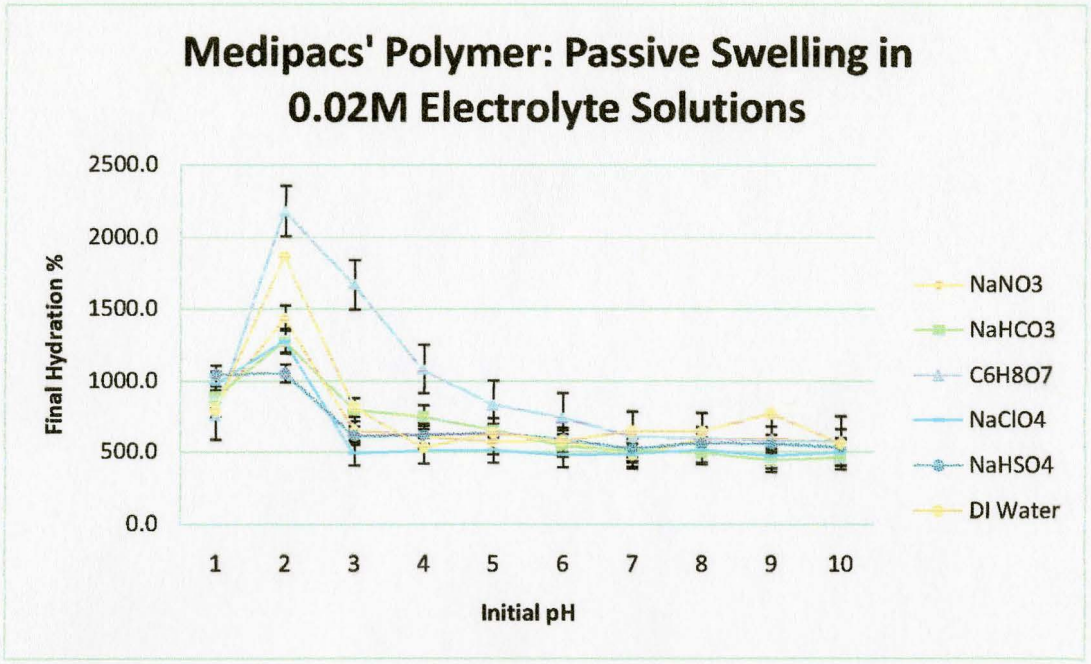

Figure 16 Medipacs' Polymer: Comparison of Passive Swelling in 0.02M Electrolyte Solutions

Table 10 Medipacs' Polymer t-test Results: Comparison of 0.02M Electrolyte Solutions to 0.02M Sodium Perchlorate Performance

T-Test Results	NaHCO3 vs. NaClO4	NaNO3 vs. NaClO4	C6H8O7 vs. NaClO4	NaHSO4 vs. NaClO4
P-Value	0.022	0.011	0.000	0.020
Significant? (95% Confidence)	Yes	Yes	Yes	Yes

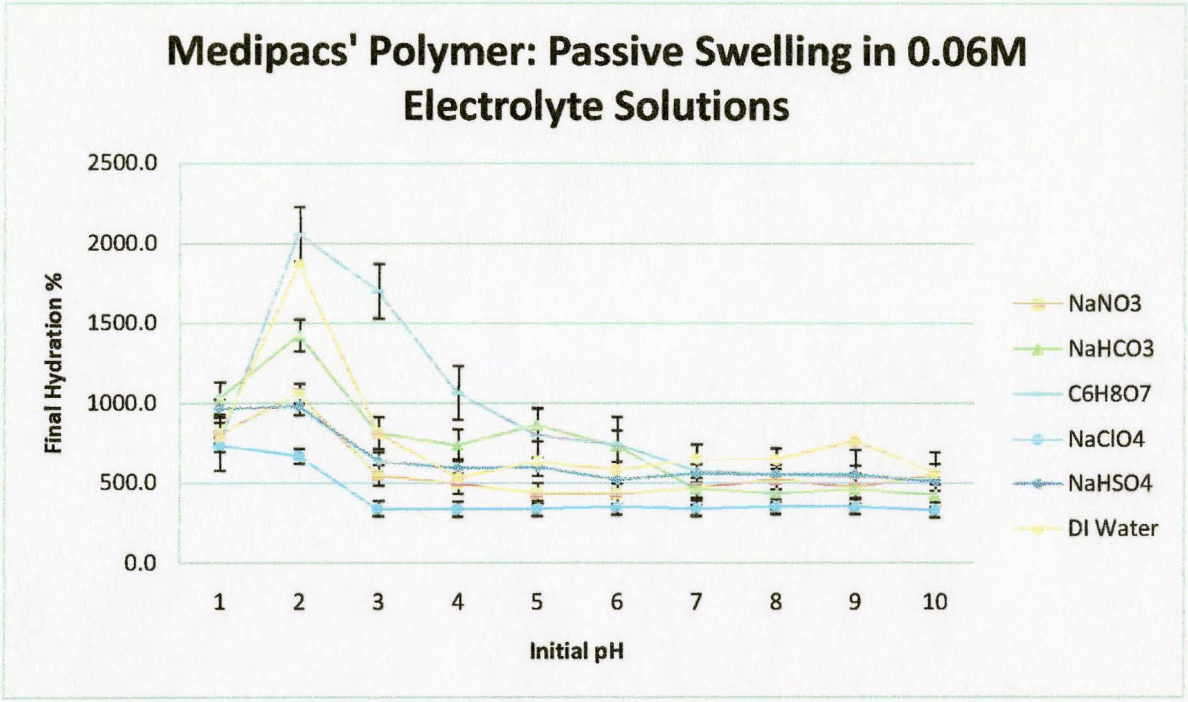

Figure 17 Medipacs' Polymer: Comparison of Passive Swelling in 0.06M Electrolyte Solutions

Table 11 Medipacs' Polymer t-test Results: Comparison of 0.06M Electrolyte Solutions to 0.06M Sodium Perchlorate Performance

T-Test Results	NaHCO3 vs. NaClO4	NaNO3 vs. NaClO4	C6H8O7 vs. NaClO4	NaHSO4 vs. NaClO4
P-Value	0.000	0.000	0.000	0.000
Significant? (95% Confidence)	Yes	Yes	Yes	Yes

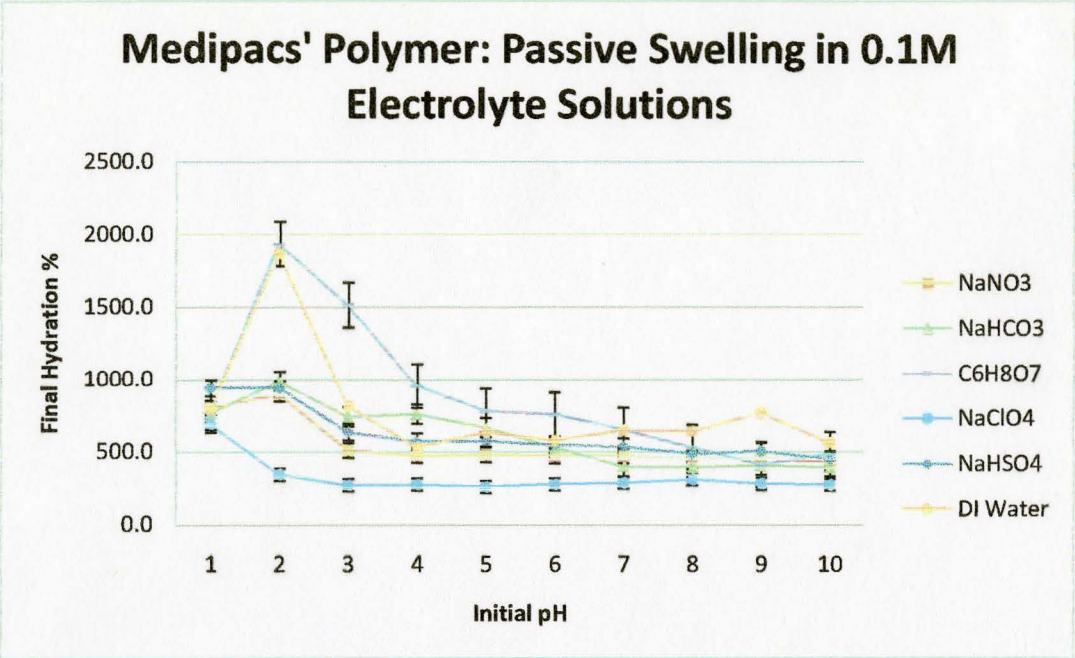

Figure 18 Medipacs' Polymer: Comparison of Passive Swelling in 0.1M Electrolyte Solutions

Table 12 Medipacs' Polymer t-test Results: Comparison of 0.1M Electrolyte Solutions to 0.1M Sodium Perchlorate Performance

T-Test Results	NaHCO3 vs. NaClO4	NaNO3 vs. NaClO4	C6H8O7 vs. NaClO4	NaHSO4 vs. NaClO4
P-Value	0.000	0.000	0.000	0.000
Significant? (95% Confidence)	Yes	Yes	Yes	Yes

3.3. Base-Swelling Polymer Passive Swelling

3.3.1. Base-Swelling Polymer Passive Swelling Experiments

3.3.1.1. Effect of Electrolyte Concentration on Hydration

Just as in Chapter 3.2.1.1., the effect of increasing concentrations of each electrolyte was established. Each electrolyte's concentration was compared with the concentration below it (0.06M was compared to 0.02M, for example), and the 0.02M concentration of the electrolyte was compared to a DI water control. The statistical analysis performed was again a 2-tail, unpaired student's t-test, which was performed in Microsoft Excel.

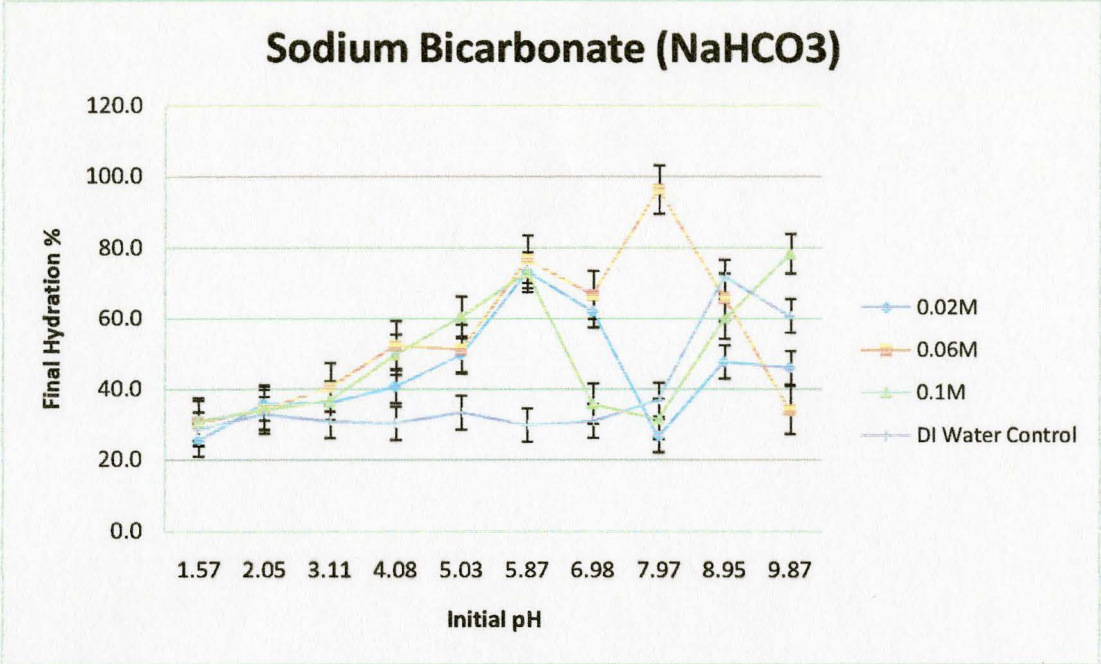

Figure 19 Base-Swelling Polymer: Sodium Bicarbonate Passive Swelling - Comparison of Differing Electrolyte Concentrations

Table 13 Base-Swelling Polymer Sodium Bicarbonate t-test Results: Comparison of Differing Electrolyte Concentrations

NaHCO3 T-Test Results	DI Water vs. 0.02M	0.02M vs. 0.06M	0.06M vs. 0.1M
P-Value	0.295	0.074	0.437
Significant? (95% Confidence)	No	Yes	No

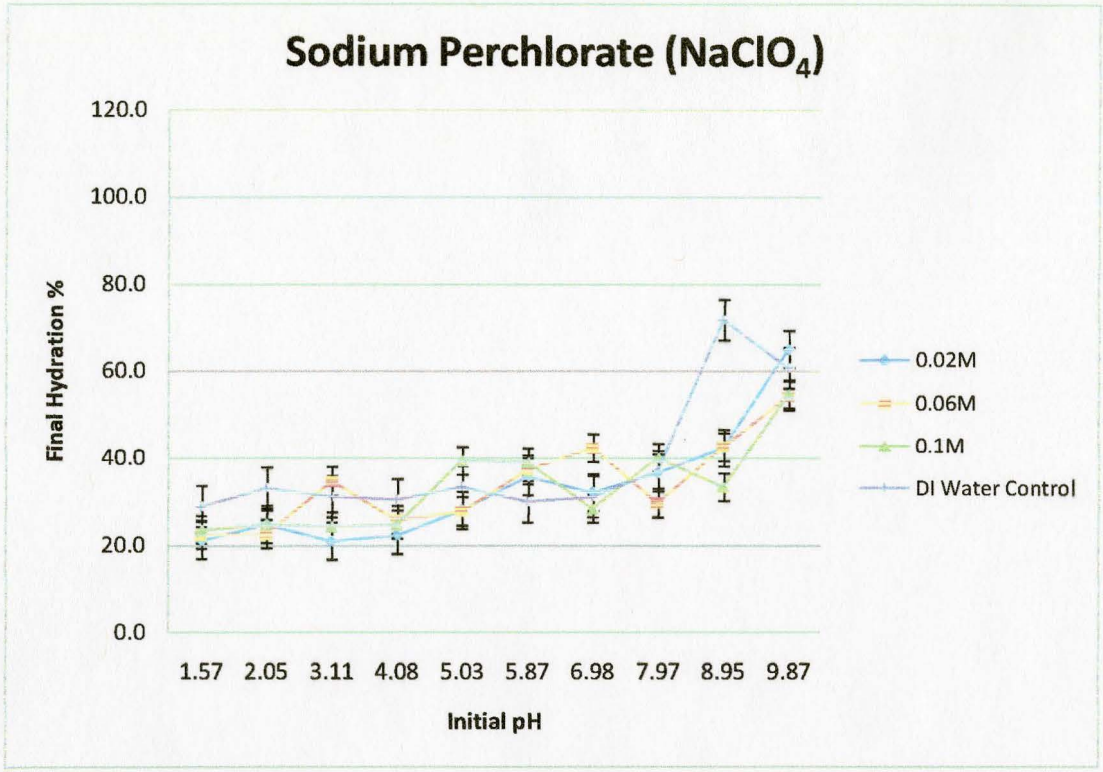

Figure 20 Base-Swelling Polymer: Sodium Perchlorate Passive Swelling - Comparison of Differing Electrolyte Concentrations

Table 14 Base-Swelling Polymer Sodium Perchlorate t-test Results: Comparison of Differing Electrolyte Concentrations

NaClO4 T-Test Results	DI Water vs. 0.02M	0.02M vs. 0.06M	0.06M vs. 0.1M
P-Value	0.083	0.573	0.799
Significant? (95% Confidence)	No	No	No

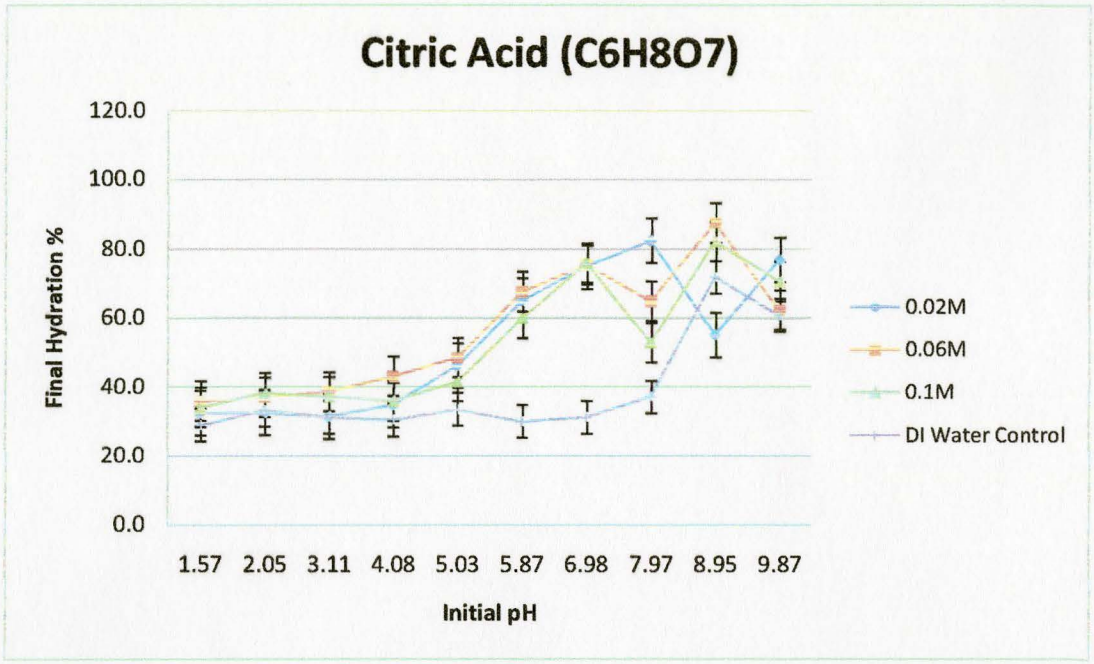

Figure 21 Base-Swelling Polymer: Citric Acid Passive Swelling - Comparison of Differing Electrolyte Concentrations

Table 15 Base-Swelling Polymer Citric Acid t-test Results: Comparison of Differing Electrolyte Concentrations

Citric Acid T-Test Results	DI Water vs. 0.02M	0.02M vs. 0.06M	0.06M vs. 0.1M
P-Value	0.003	0.368	0.038
Significant? (95% Confidence)	Yes	No	Yes

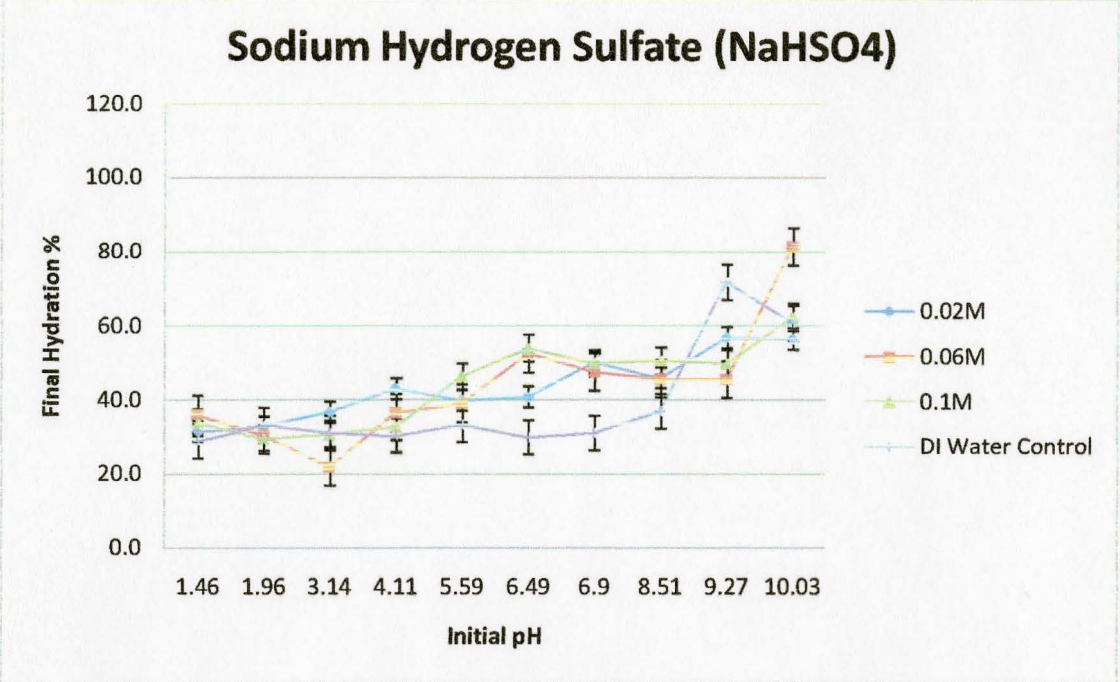

Figure 22 Base-Swelling Polymer: Sodium Hydrogen Sulfate Passive Swelling - Comparison of Differing Electrolyte Concentrations

Table 16 Base-Swelling Polymer Sodium Hydrogen Sulfate t-test Results: Comparison of Differing Electrolyte Concentrations

NaHSO4 T-Test Results	DI Water vs. 0.02M	0.02M vs. 0.06M	0.06M vs. 0.1M
P-Value	0.042	0.913	0.868
Significant? (95% Confidence)	Yes	No	No

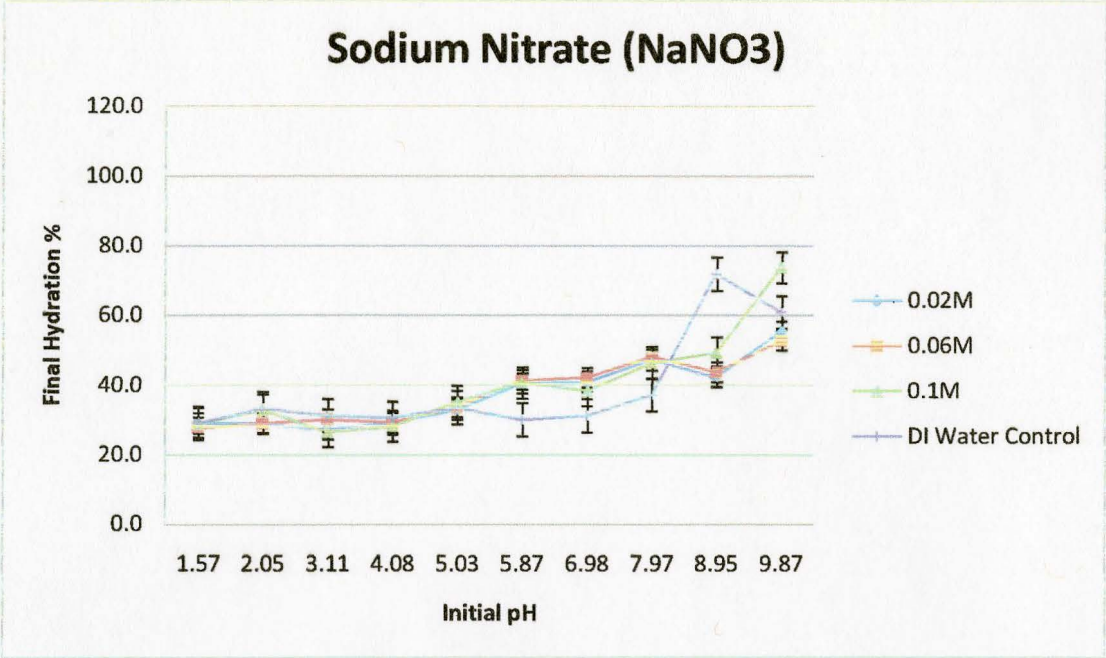

Figure 23 Base-Swelling Polymer: Sodium Nitrate Passive Swelling - Comparison of Differing Electrolyte Concentrations

Table 17 Base-Swelling Polymer Sodium Nitrate t-test Results: Comparison of Differing Electrolyte Concentrations

NaNO3 T-Test Results	DI Water vs. 0.02M	0.02M vs. 0.06M	0.06M vs. 0.1M
P-Value	0.636	0.737	0.229
Significant? (95% Confidence)	No	No	No

3.3.1.2. Comparison of the Hydration Abilities of Different Electrolytes

Just as in Chapter 3.2.1.2., a comparison of each electrolyte was made relative to sodium perchlorate (the original electrolyte) at each concentration, but this time the base-swelling gel was compared. As an example, all electrolytes were compared to sodium perchlorate at a concentration of 0.02M, and then a separate comparison was performed at 0.06M (and so on). The same Excel t-test as in section 3.2.1.1 (above) was run for each comparison. (As a reminder, the t-test is an unpaired, 2-tail t-test).

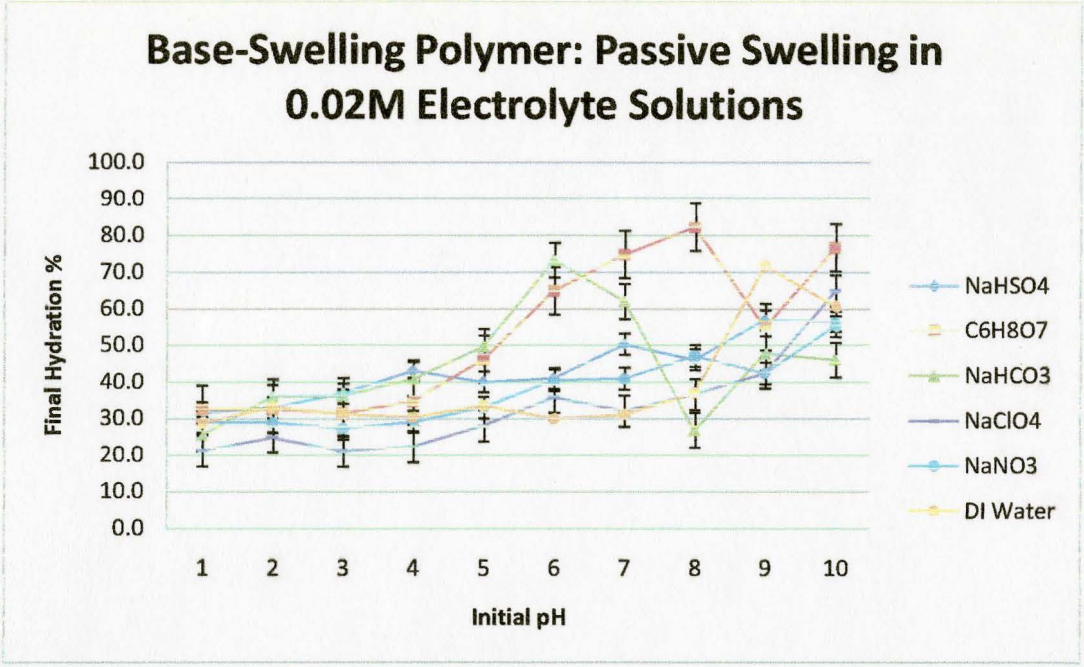

Figure 24 Base-Swelling Polymer: Comparison of Passive Swelling in 0.02M Electrolyte Solutions

Table 18 Base-Swelling Polymer t-test Results: Comparison of 0.02M Electrolyte Solutions to 0.02M Sodium Perchlorate Performance

T-Test Results	NaHCO3 vs. NaClO4	NaNO3 vs. NaClO4	C6H8O7 vs. NaClO4	NaHSO4 vs. NaClO4
P-Value	0.014	0.002	0.000	0.000
Significant? (95% Confidence)	Yes	Yes	Yes	Yes

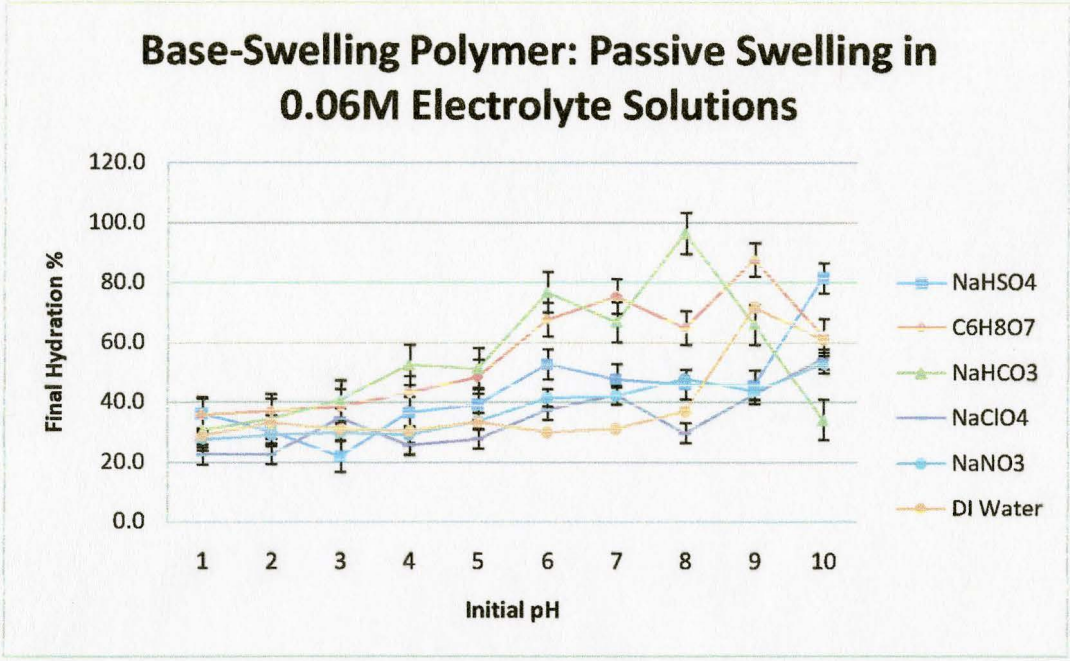

Figure 25 Base-Swelling Polymer: Comparison of Passive Swelling in 0.06M Electrolyte Solutions

Table 19 Base-Swelling Polymer t-test Results: Comparison of 0.02M Electrolyte Solutions to 0.06M Sodium Perchlorate Performance

T-Test Results	NaHCO3 vs. NaClO4	NaNO3 vs. NaClO4	C6H8O7 vs. NaClO4	NaHSO4 vs. NaClO4
P-Value	0.001	0.179	0.000	0.002
Significant? (95% Confidence)	Yes	No	Yes	Yes

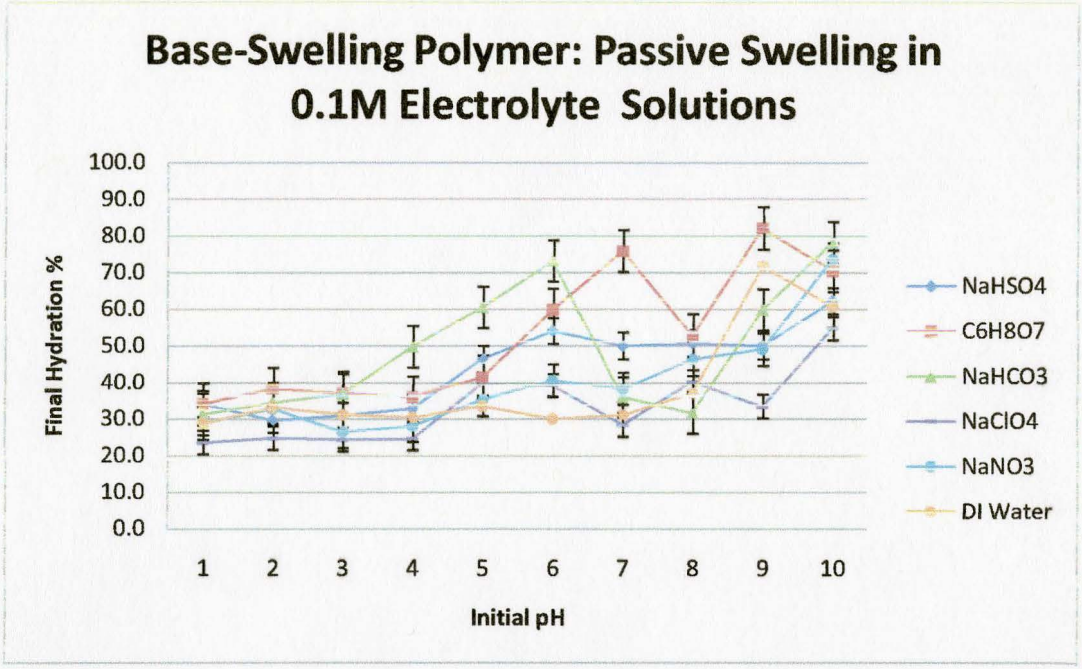

Figure 26 Base-Swelling Polymer: Comparison of Passive Swelling in 0.1M Electrolyte Solutions

Table 20 Base-Swelling Polymer t-test Results: Comparison of 0.02M Electrolyte Solutions to 0.1M Sodium Perchlorate Performance

T-Test Results	NaHCO3 vs. NaClO4	NaNO3 vs. NaClO4	C6H8O7 vs. NaClO4	NaHSO4 vs. NaClO4
P-Value	0.000	0.000	0.000	0.000
Significant? (95% Confidence)	Yes	Yes	Yes	Yes

3.4. Active Swelling Experiments

3.4.1. Base-Swelling Polymer

3.4.1.1. Effect of Electrolyte Concentration on Swelling

Linear regression analysis via Microsoft Excel's data analysis toolbox was used on each curve gathered during active swelling, and a trend line was established for each graphed curve. The swelling was measured as increase (or decrease) in distance (millimeters) during the 30 minutes of active swelling. Due to a theoretical starting point (curve's y-intercept) of zero-millimeters, the regression analysis variables analyzed were the R^2 value of each curve

and the slope of each curve. The R^2 value serves as a measure of the ability of the regression equation's ability to predict the distribution of the graphed points; for example, if an R^2 value of 1.0 is produced, then the points measured via regression form a perfect line. The lower the R^2 value for the curve, the worse the linear fit of the data points, and, consequentially, the less reliable the data gathered during the experiment. The slope of the lines $(\frac{Polymer\ Expansion\ Distance}{Time})$ helps to determine the speed of polymer expansion during the test, and also allows the effect of the different electrolytes to be determined.

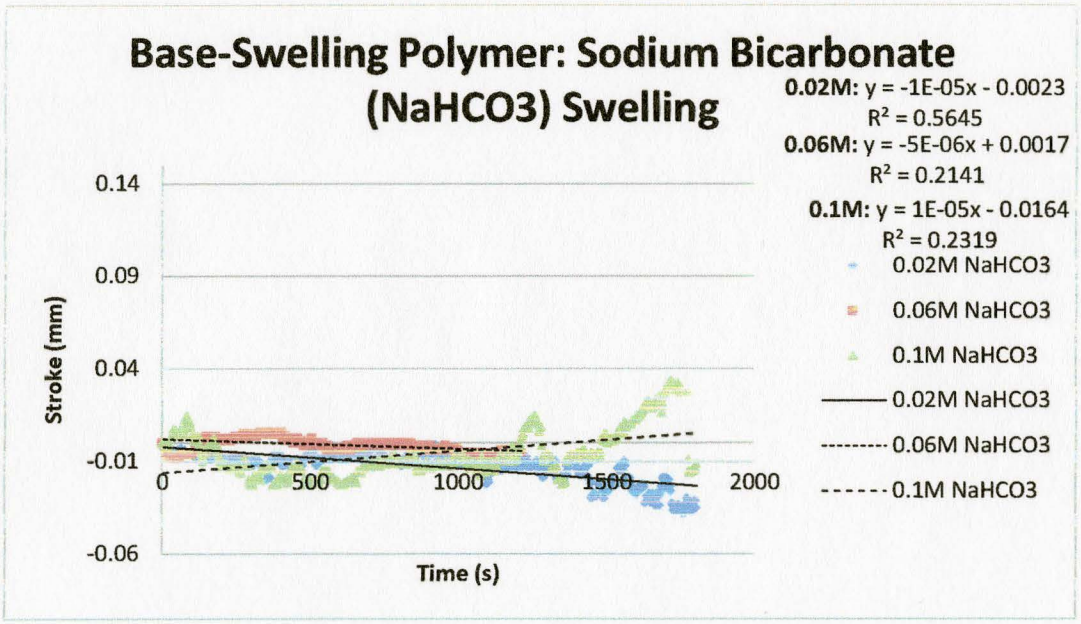

Figure 27 Base-Swelling Polymer Active Swelling: Sodium Bicarbonate

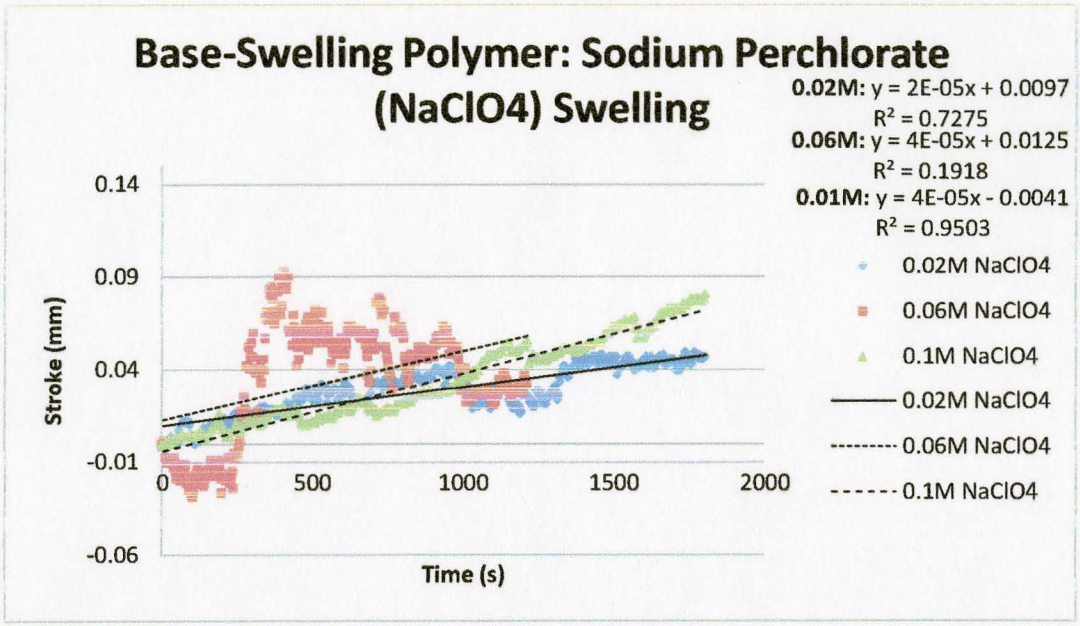

Figure 28 Base-Swelling Polymer Active Swelling: Sodium Perchlorate

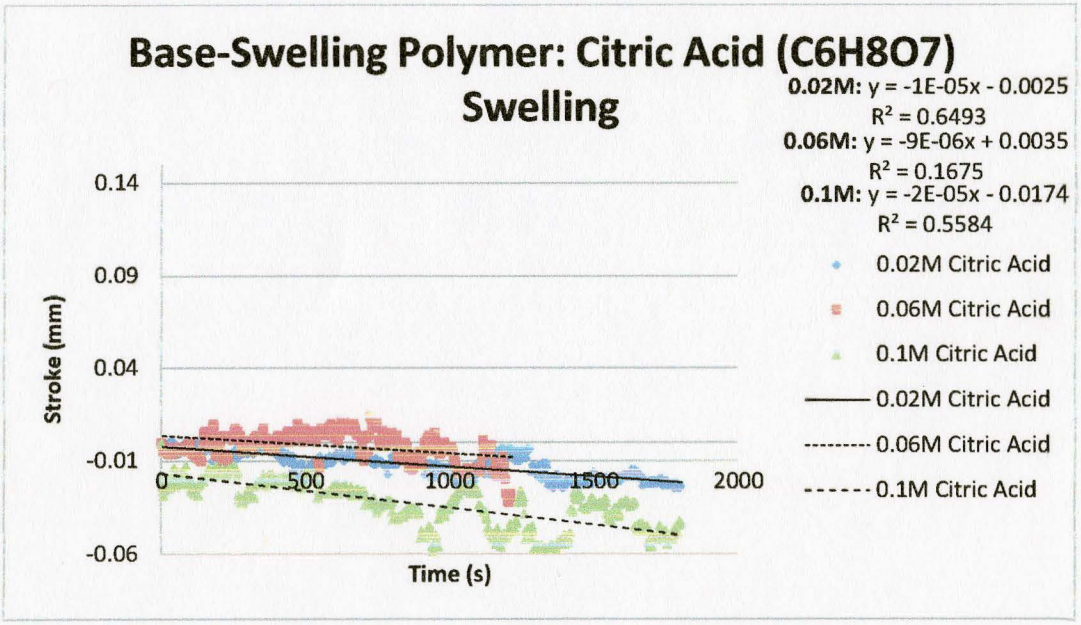

Figure 29 Base-Swelling Polymer Active Swelling: Citric Acid

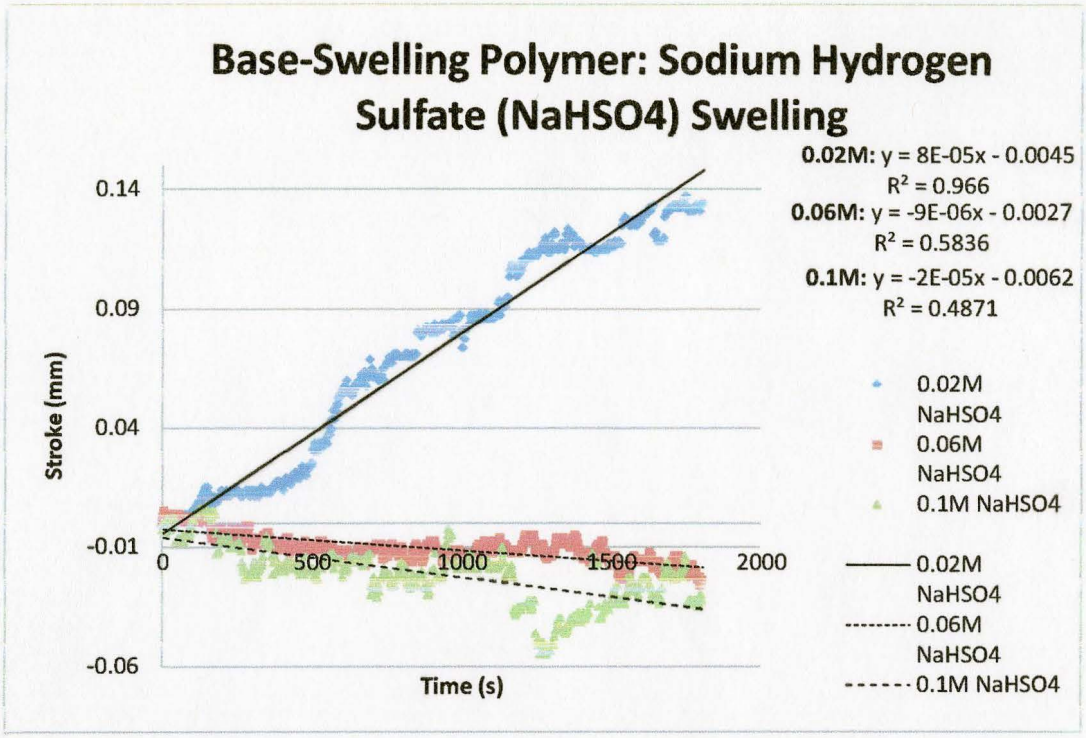

Figure 30 Base-Swelling Polymer Active Swelling: Sodium Hydrogen Sulfate

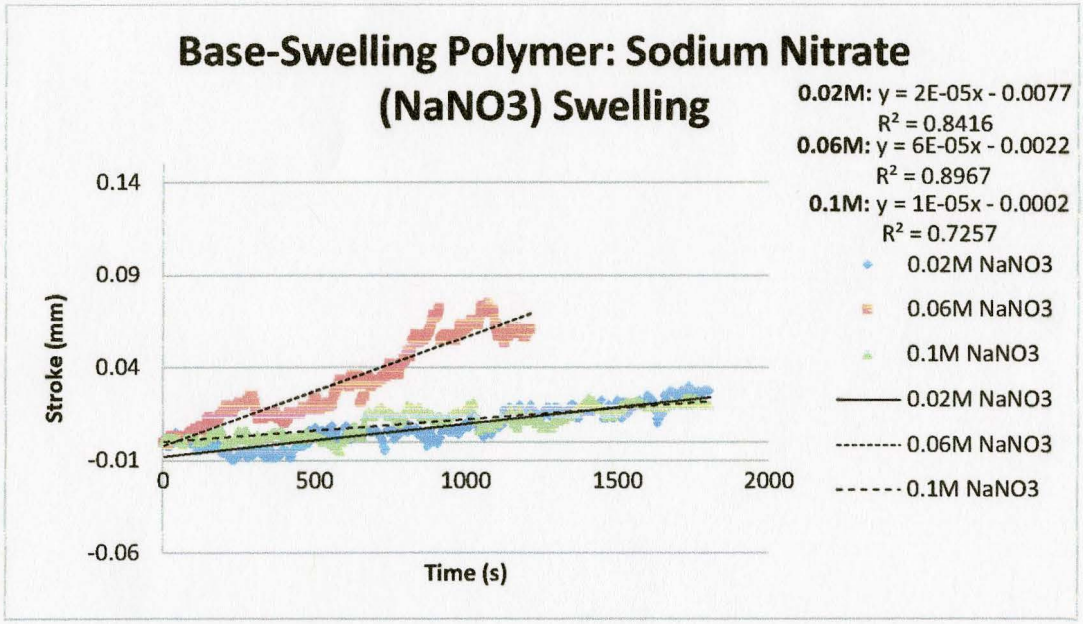

Figure 31 Base-Swelling Polymer Active Swelling: Sodium Nitrate

3.4.1.2. Comparison of the Hydration Abilities of the Different Electrolytes

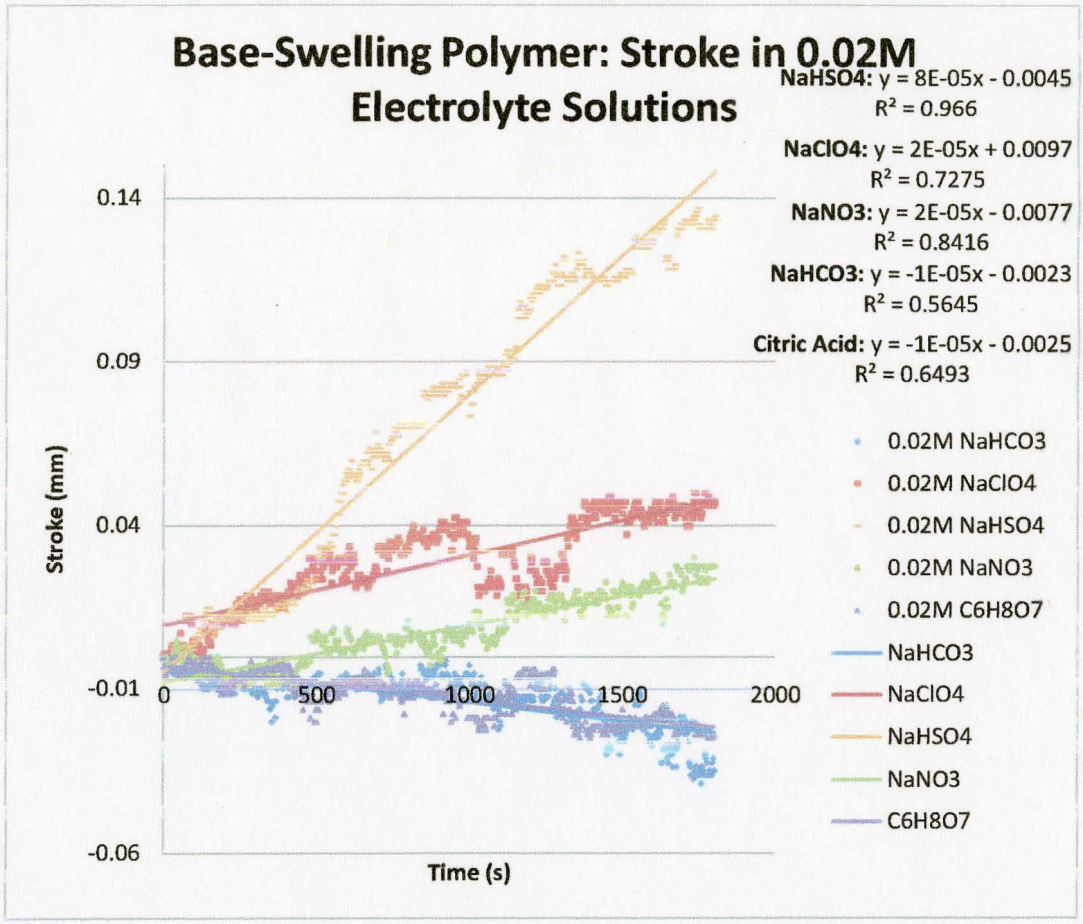

Figure 32 Base-Swelling Polymer Active Swelling: 0.02M Electrolyte Concentration Comparison

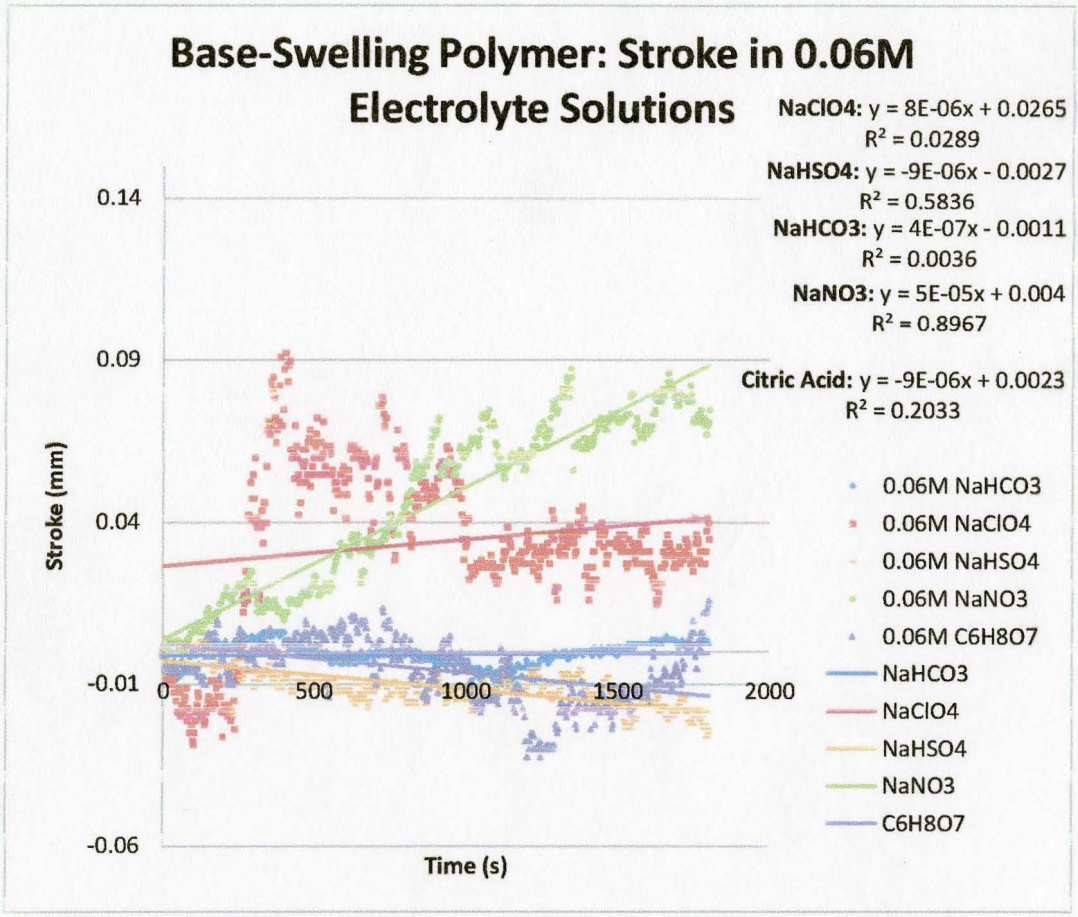

Figure 33 Base-Swelling Polymer Active Swelling: 0.06M Electrolyte Concentration Comparison

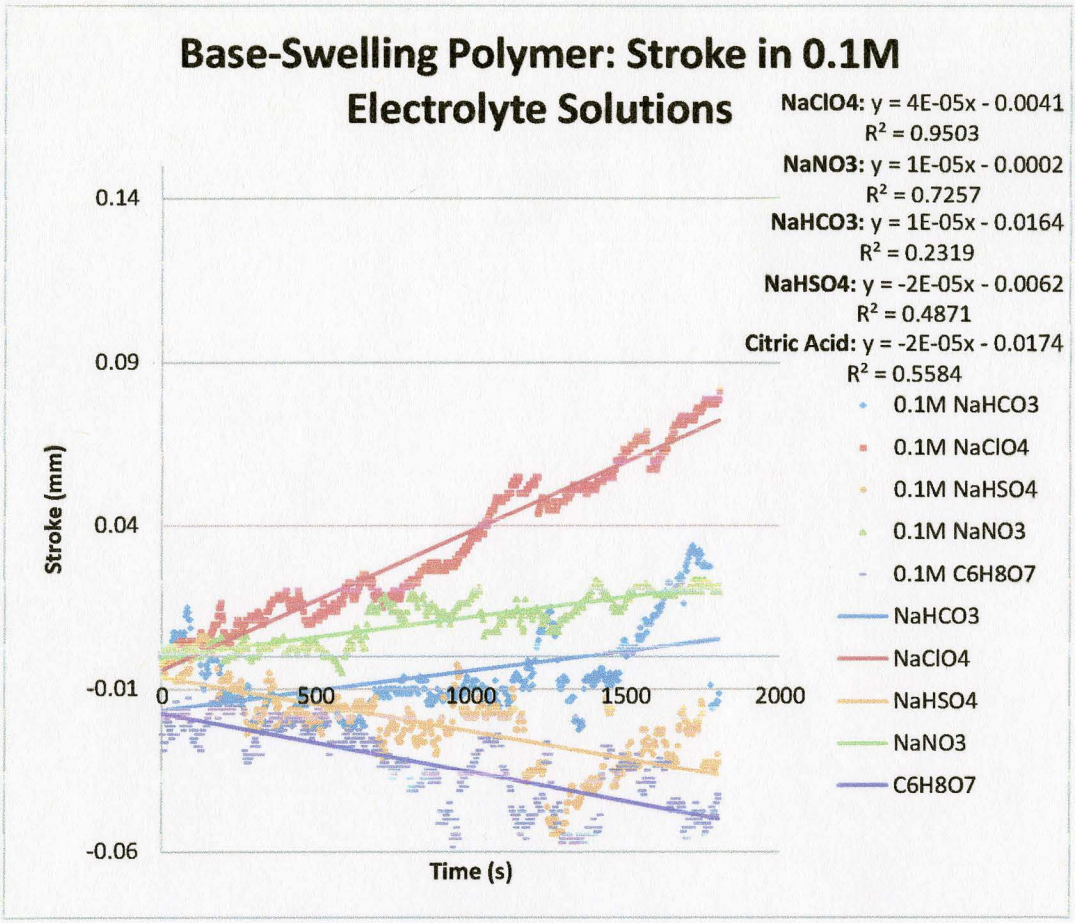

Figure 34 Base-Swelling Polymer Active Swelling: 0.1M Electrolyte Concentration Comparison

3.4.2. Medipacs' Polymer

3.4.2.1. Effect of Electrolyte Concentration on Swelling

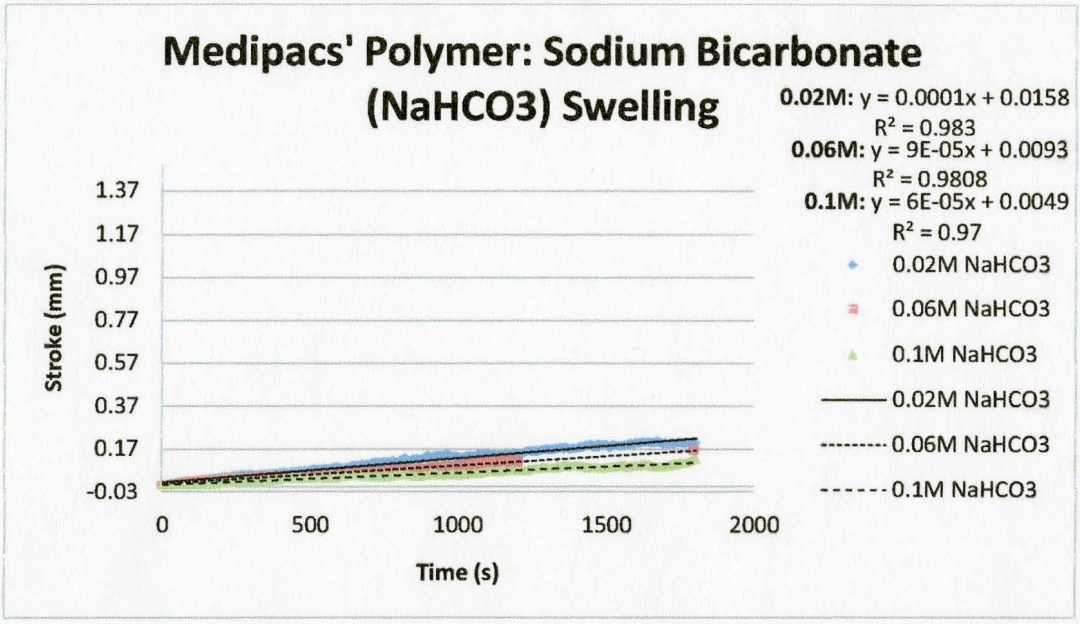

Figure 35 Medipacs' Polymer Active Swelling: Sodium Bicarbonate

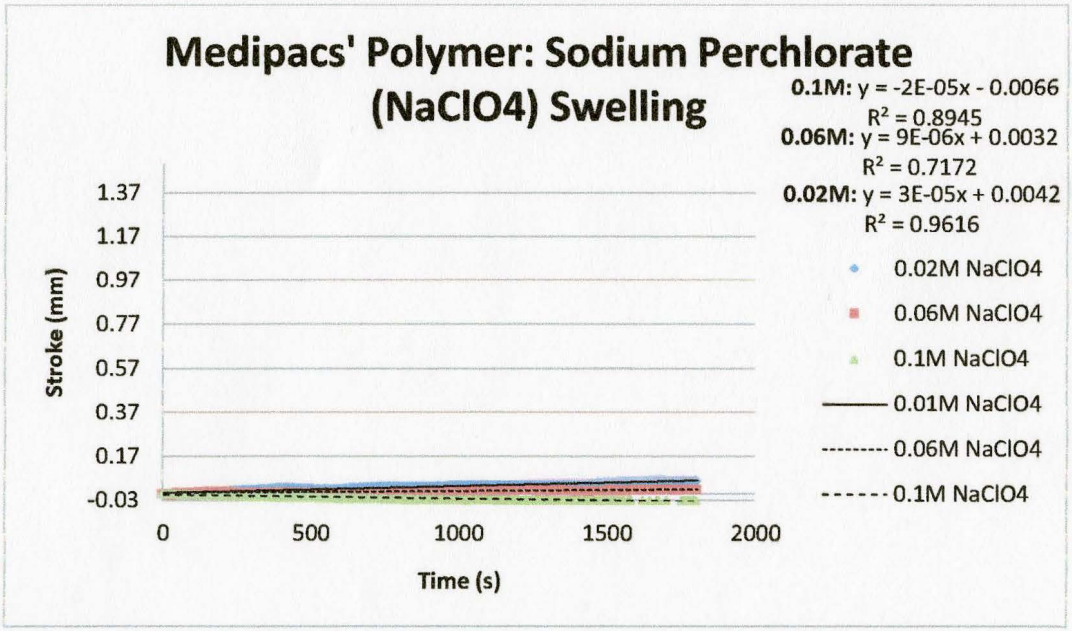

Figure 36 Medipacs' Polymer Active Swelling: Sodium Perchlorate

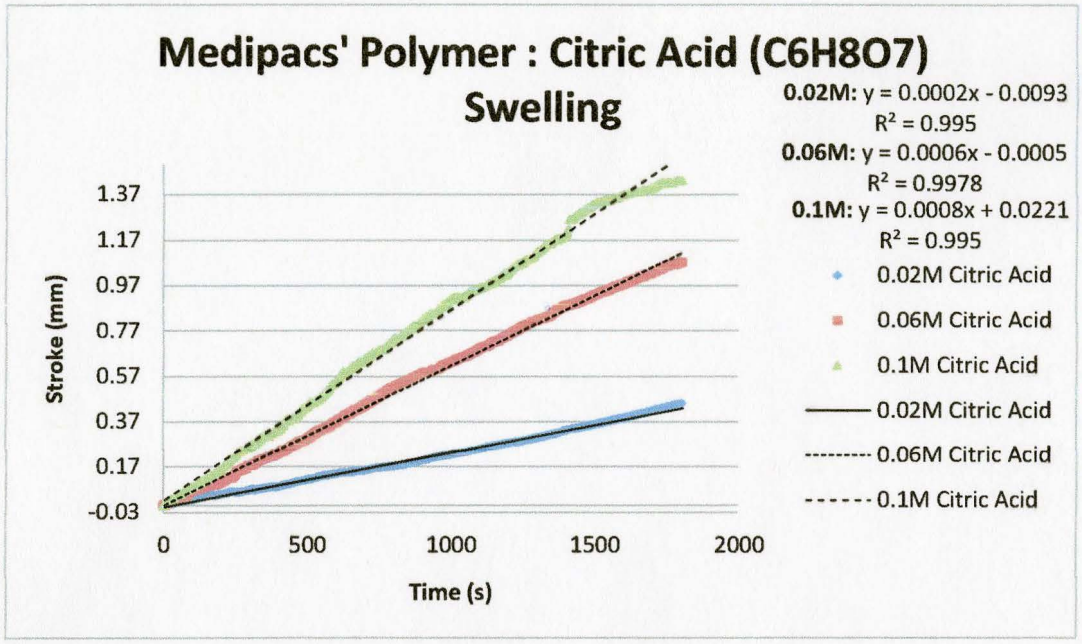

Figure 37 Medipacs' Polymer Active Swelling: Citric Acid

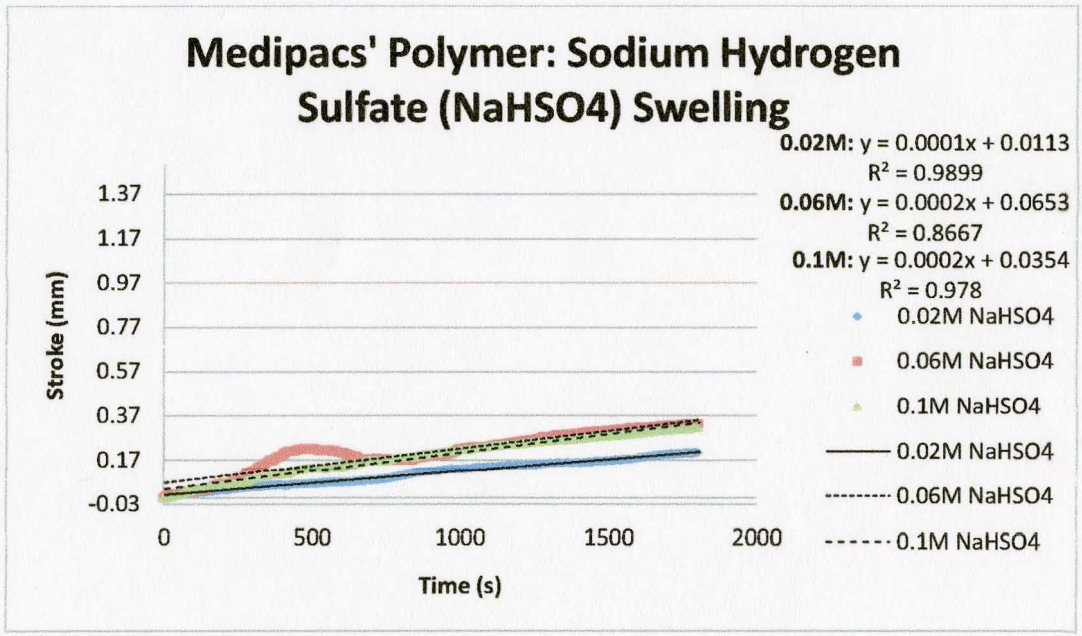

Figure 38 Medipacs' Polymer Active Swelling: Sodium Hydrogen Sulfate

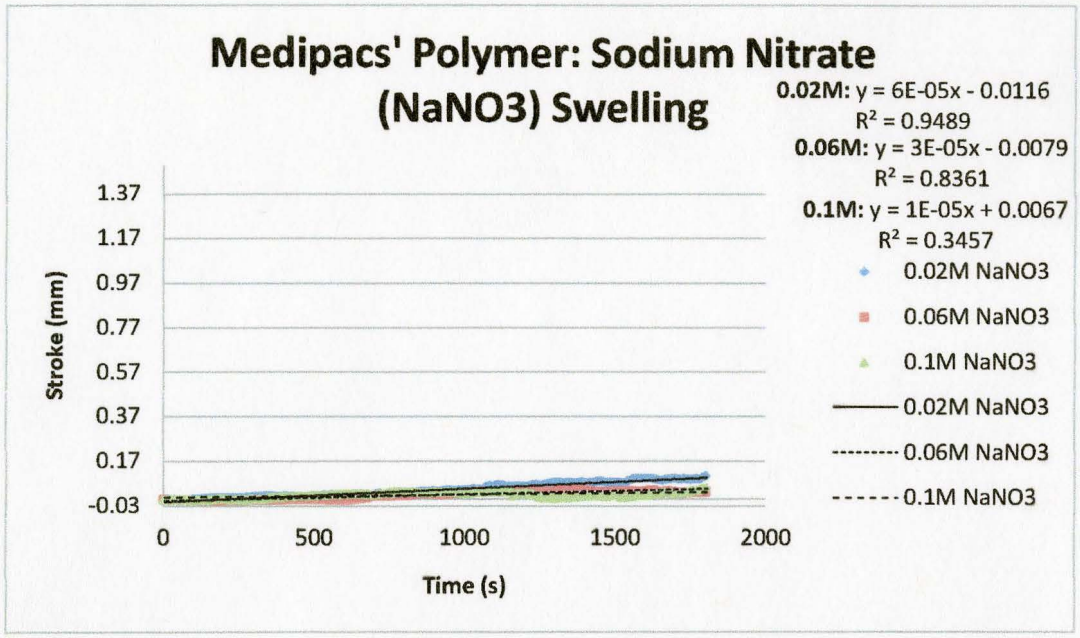

Figure 39 Medipacs' Polymer Active Swelling: Sodium Nitrate

3.4.2.2. Comparison of the Hydration Abilities of the Different Electrolytes

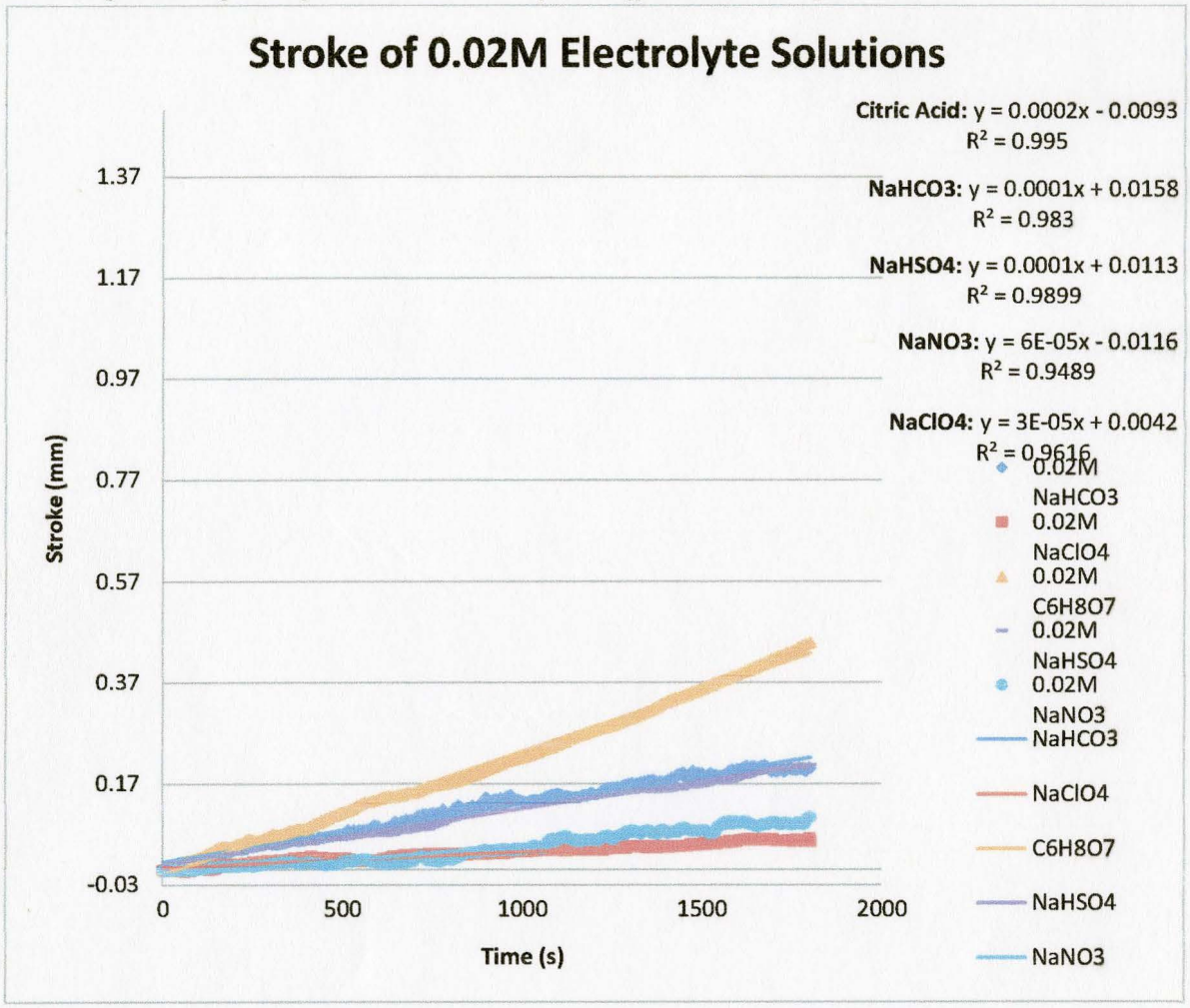

Figure 40 Medipacs' Polymer Active Swelling: 0.02M Electrolyte Concentration Comparison

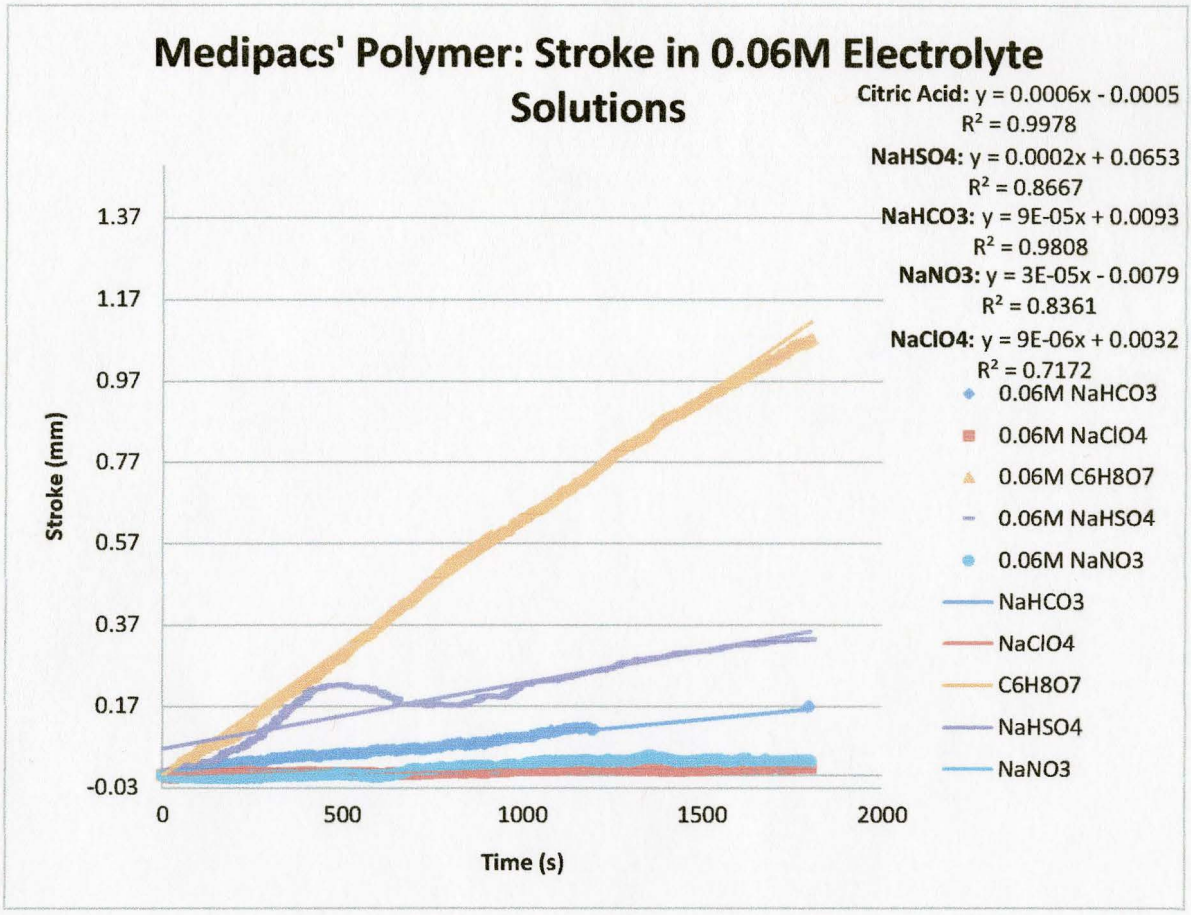

Figure 41 Medipacs' Polymer Active Swelling: 0.06M Electrolyte Concentration Comparison

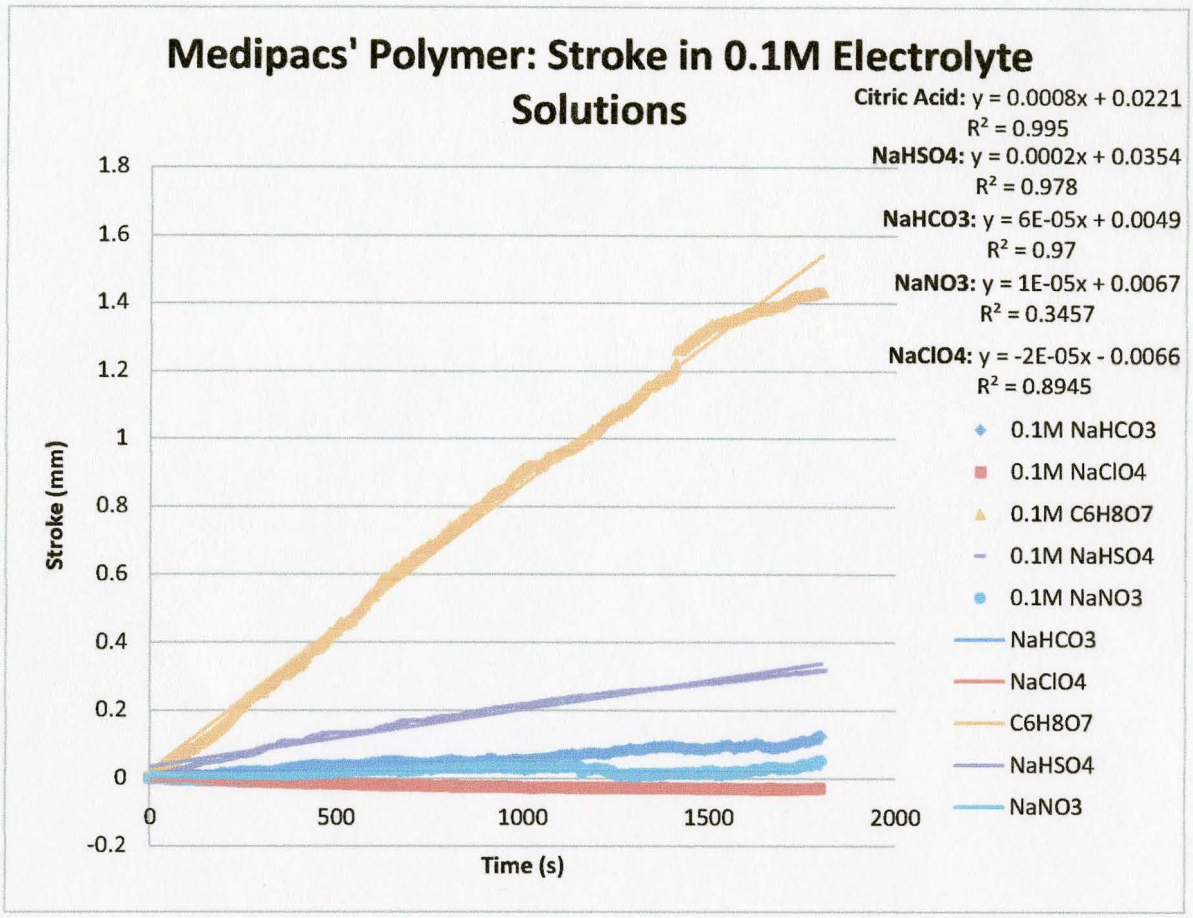

Figure 42 Medipacs' Polymer Active Swelling: 0.1M Electrolyte Concentration Comparison

4. Discussion

4.1. Passive Swelling

4.1.1. Medipacs' Polymer: Comparison of the Hydration Abilities of Different Electrolytes

For Medipacs' polymer, the results from this study confirmed that sodium bicarbonate far outperforms sodium perchlorate during passive swelling. The passive swelling experiments were measured over a period of time long enough to confirm that the polymer had reached its peak swelling level, although this data is not shown (supplementary data). As expected, Medipacs' polymer's maximum swelling decreased as the concentration of electrolyte increased; this rang

true for each electrolyte. An electrolyte concentration that is too high is expected to block the ability of the positive charges on Medipacs' polymer's matrix to "see" each other and repel away from each other, causing expansion; in addition, a concentration of electrolyte that is too high is expected to cause a "negative" osmotic pressure, where solvent (water) exits the polymer's matrix.

Not only did sodium perchlorate hinder swelling as its concentration increased, but Medipacs' polymer's swelling was lowest in sodium perchlorate solution for every concentration and at every pH (except at a concentration of 0.02M for a pH of 1, 2, 9, and 10). Also as expected, sodium nitrate's swelling performance is similar to, but slightly better than, sodium perchlorate at all pH levels. Although sodium nitrate's swelling performance is better than sodium perchlorate overall, it still consistently fails to reach a hydration percentage above 500% for concentrations of 0.06M and 0.1M and a pH of 4 and above; it also fails to reach a hydration percent of 1500% and above for acidic conditions. The low swelling rate during passive swelling by both sodium nitrate and sodium perchlorate supports the hypothesis that an electrolyte able to donate a hydrogen ion to the solution will improve the swelling because neither electrolyte (sodium perchlorate or sodium nitrate) contains a hydrogen ion.

The three best performing electrolytes, sodium hydrogen sulfate, sodium bicarbonate and citric acid all either have constituents that act as hydrogen-carriers or are able to donate their own hydrogen ions to the system. Sodium bicarbonate's bicarbonate ion, as previously discussed, forms water and carbon-dioxide gas in an acidic environment; in turn, the carbon dioxide naturally picks up hydrogen ions to form a HCOOH molecule in solution with a standard electrode potential of -0.11 (see: Table 3). The carbon dioxide can then transport the hydrogen ions in the electrolyte solution to the polymer.

Sodium hydrogen sulfate and citric acid both carry hydrogen atoms that can be donated to the solution. As previously discussed, citric acid was evaluated specifically due to its ability to donate multiple hydrogen ions to the solution; citric acid, along with other chemicals with multiple donatable hydrogen ions (and, consequentially, multiple pK_a values) are known as polyprotic chemicals. As expected, citric acid electrolyte solutions not only produced a greater swelling effect during passive swelling on Medipacs' polymer at a pH of about 2, compared with all other electrolyte solutions and DI water; however, the citric acid electrolyte solutions also buffered the swelling effect of the polymer at all acidic pH levels. This is expected due to citric acid's three pK_a values: 6.41, 4.75, and 3.09. At each a pH corresponding to each pK_a value, citric acid will lose a hydrogen atom; therefore, it can act as a type of buffer for the solution. While these findings are very positive, there are more experiments that must be performed on the electrolyte solutions in order to confirm citric acid's ability to increase swelling on Medipacs' polymer at a wide pH range due to the buffering effect. The concern in citric acid, partially due to its buffering qualities, is its ability to control the swelling of the polymer to the extent that it can swell in an on-off pattern, which is important in controlling infusion pumps and in medication delivery—two areas of research for Medipacs.

Sodium hydrogen sulfate has a lower pK_a value, 1.99, so its hydrogen atom is expected to dissociate and keep an equilibrium pH of about 1.99 in solution. Interestingly, sodium hydrogen sulfate was the only electrolyte solution to exhibit equal swelling at a pH of one and pH of two; this is possibly due to the sulfate ion's ability to pick up hydrogen ions and form sulfurous acid (H_2SO_4), consequentially buffering the solution (similarly to citric acid). Therefore, it is also recommended that more evaluation be performed on the sodium hydrogen sulfate to evaluate its efficacy as an electrolyte.

As for the statistical analysis performed, the t-test analysis showed that every electrolyte solution, when compared to sodium perchlorate, produced a swelling result at all pH levels that was significantly higher than the sodium perchlorate swelling result. The statistical analysis also showed that increasing the concentration of electrolyte produced a significant difference in swelling for every electrolyte and every concentration, except for two instances; the citric acid and the sodium bicarbonate responses were not significantly different when the concentration was increased from 0.02M to 0.06M. The lack of a statistical difference in performance during passive swelling indicates that the lower concentration (0.02M) should be used for citric acid and sodium bicarbonate in order to conserve reagent, if a choice must be made between 0.06M and 0.02M concentrations.

4.1.2. Base-Swelling Polymer: Comparison of the Hydration Abilities of Different Electrolytes

Overall, the base-swelling polymer did not swell very much at all in comparison to Medipacs' polymer, although this was expected. The difference between the swelling amounts produced between two different electrolytes was at most 20%, and the electrolytes never produced a swelling amount over 100% at any pH and for any electrolyte.

Overall, the base-swelling polymer's swelling ability did not seem to change when the electrolyte concentration increased, and this was confirmed with the statistical t-test analysis performed. The only two instances of relevance where a statistical difference was seen for increasing concentration occurred during an increase from 0.06M to 0.1M citric acid and from DI water (no electrolyte) to 0.02M citric acid. Citric acid's buffering effect is once again seen, although this time it is seen for the base-swelling polymer and at a high pH level; again, the buffering effect that citric acid brings up raises the concern that the pH of the solution during electrical application may not be controllable.

The other interesting find during base-swelling polymer passive swelling came with the sodium bicarbonate electrolyte solution. Noticeably, the results for sodium bicarbonate did not show a consistent increase in swelling as the pH level increased, as was expected. When acid was added to adjust the pH of the solution during the experiment for the pH levels below 7, a great amount of gas bubbles were observed bubbling out of solution; given the reaction formula of sodium bicarbonate and hydrogen ($H^+ + HCO3^- \leftrightarrow H_2O + CO_2$) (Vyalykh, Dubinov, L'vov, Sadovoy, & Selemir, 2010), these bubbles are theoretically expected to be carbon dioxide gas forming in solution. Understandably, the sodium bicarbonate electrolyte solutions at pH levels above 7 did not show carbon dioxide gas forming; however, the base-swelling polymer's matrix includes an acrylic acid monomer, which, when the polymer takes on the electrolyte solution, theoretically reacted with the bicarbonate ion as an acid to produce carbon dioxide gas. Not only did the base-swelling polymer break apart as it took on electrolyte solution, making measurements difficult, but intact polymers had gas bubbles attached to them when they were pulled out of solution; it is theorized that the attached gas bubbles are also carbon dioxide bubbles due to the acrylic acid reacting with the sodium bicarbonate electrolyte.

The formation of carbon dioxide gas is as big of a concern in electrolyte formation as is the buffering capability of citric acid because gas formation in a polymer bag placed into an infusion pump can also hinder the polymer's ability to expand in a manner controllable enough to deliver boluses of drugs to infusion pump patients.

The sodium hydrogen sulfate electrolyte did not exhibit a buffering effect during the passive swelling of the base-swelling polymer, suggesting the possibility that it may be a more reliable electrolyte for use than citric acid. In fact, for both the base-swelling polymer and Medipacs' polymer, sodium hydrogen sulfate showed the most promising results because it

induced swelling levels higher than sodium bicarbonate, but it did not buffer the solution as citric acid did; sodium hydrogen sulfate did not produce swelling levels as high as citric acid, though. It is therefore recommended that more experiments be performed on sodium hydrogen sulfate to further evaluate its efficacy as an electrolyte.

4.2. Active Swelling

None of the electrolytes tested degraded under the voltages at which the experiment was run (this can be seen in Table 3 in Chapter 1.2.2.3.); however, as is important for swelling, water did degrade under swelling and therefore contributed a hydrogen atom (for the swelling experiments for Medipacs' polymer) or a hydroxide ion (for the swelling experiments for the base-swelling polymer).

4.2.1. Medipacs' Polymer: Comparison of the Swelling Capabilities of Different Electrolytes

Each graph in the results section is displayed with the same axis in order to better show the relative swelling capabilities of each electrolyte. Upon examination, two major observations stand out. First, citric acid far outperforms all other electrolytes, while sodium hydrogen sulfate has modest performance (although its performance comes nowhere near citric acid's performance). Second, the non-hydrogen-donating electrolytes caused a decrease in swelling as their concentration was increased, while the hydrogen-donating electrolytes (sodium hydrogen sulfate and citric acid) caused an increase in swelling as their concentration was increased. Both of these results were expected at the onset of the experiment. That citric acid produces a swelling rate that is roughly three times that of sodium hydrogen sulfate may be directly due to its ability to donate three hydrogen ions to the reaction system, while sodium hydrogen sulfate can only donate one hydrogen ion. It is possible that free hydrogen ions in the solution overpower the other ions in the solution, such as the citrate ion for citric acid and the sulfate ion in sodium hydrogen sulfate, based on the results obtained for citric acid and sodium hydrogen sulfate.

The non-hydrogen donating electrolytes also produced expected results. At each concentration, sodium perchlorate caused the lowest swelling rate, and it even produced a negative swelling rate at its highest concentration, 0.1M. Sodium nitrate caused the second-lowest swelling rate, just barely above sodium perchlorate's, as is predicted from its standard electrode potential.

Sodium bicarbonate also produced an expected swelling rate, a swelling rate lower than that for the hydrogen-donating electrolytes, but higher than that for sodium perchlorate and sodium nitrate. Sodium bicarbonate, due to its ability to form carbon dioxide gas upon contact with an acid, is not a true hydrogen donator for the reaction; instead, the carbon dioxide picks up hydrogen molecules in solution and acts as a hydrogen carrier to transport the hydrogen molecules to the polymer's matrix.

4.2.2. Base-Swelling Polymer: Comparison of the Swelling Capabilities of Different Electrolytes

Although the electrode polarity was reversed to produce a basic environment for the base-swelling polymer, the base-swelling polymer did not swell much at all: only 0.14mm at its most for 0.02M sodium hydrogen sulfate. This low swelling rate resulted in a large amount of noise in the system, likely produced from the laser used to measure the swelling rate of the polymers.

Despite the low swelling rate, the results, interestingly, seemed to deviate from the results obtained during the passive swelling experiments. According to the passive swelling experiments, the citric acid and sodium hydrogen sulfate electrolytes were expected to produce slightly better results than the other electrolyte solutions; however, neither produced promising results overall. Citric acid produced negative swelling results each time, although the hydrogen

ions that it carries may have impeded the base-swelling polymer's ability to swell by shielding the polymer's negative O^- charges from each other or by preventing the hydrogen ions from being pulled off of the OH^- groups in the polymer in the first place. Sodium hydrogen sulfate also produced negative swelling results for its 0.06M and 0.1M concentrations, possibly for the same reasons that citric acid produced poor swelling results. Sodium hydrogen sulfate did, however, produce the best swelling result for the base-swelling polymer of all of the electrolytes tested; at 0.02M, sodium hydrogen sulfate caused the polymer to swell up to 0.14mm.

Interestingly, the non-hydrogen-donating electrolytes, sodium nitrate and sodium perchlorate, had the best overall results for the base-swelling polymer at every concentration. Even at 0.02M, where sodium hydrogen sulfate was the best electrolyte, sodium perchlorate and sodium nitrate were clearly the second and third best electrolytes, respectively. Without performing more experiments, comparing the active swelling experiments of the base-swelling polymer to the active swelling experiments of Medipacs' polymer is difficult, due to the noisy signal involved in the measurements for the base-swelling polymer. However, the fact that the non-hydrogen-donating electrolytes outperformed the hydrogen-donating electrolytes for the base-swelling polymer 's experiments is particularly interesting because it is the reverse of the performance of the electrolytes during the experiments with Medipacs' polymer. As previously discussed, the base-swelling polymer experiments help to reinforce the relationship of the hydrogen ion in the reaction system; however, the base-swelling polymer's results also suggest that the ability of an electrolyte with negative charge to attract hydrogen molecules in an oxidation reaction, as perchlorate and nitrate can, may actually decrease its ability ablility to perform in an acidic environment and increase its ability to perform in a basic environment. More experiments are needed to confirm this suggestion.

4.3. Future Directions

Some future experiments are recommended in order to fully understand the impact of electrolytes on Medipacs' polymer. First, the electrolytes should be tested for their degradation abilities, both with Medipacs' polymer itself and with the aluminum electrode used to swell the polymer. For example, despite the positive ability of citric acid and sodium hydrogen sulfate to increase Medipacs' polymer's swelling abilities, they will be unusable if they degrade the polymer. It is important to note that, at least for one week in solution, no degradation in Medipacs' polymer was observed; however, this may not be true during long-term storage (months) or for the aluminum electrode used to apply voltage to the polymer.

Secondly, the active swelling experiments should be repeated to measure the actual, rather than the relative, swelling rates. The active swelling experiments in this report were performed after first swelling the polymer actuators in DI water before being placed into the active-swelling reaction system with the electrolyte to be tested; this was done because the electrolyte solutions will passively swell the polymer to anywhere from 400% to 2000% before actuation, which may affect the polymer's ability to swell. If the polymer is pre-swelled in DI water, then the starting polymer size for all electrolytes will be the same, although some passive swelling will be observed during the active swelling experiment. To counteract this, the same active swelling experiments should be repeated, but without the application of voltage. In order to obtain the true swelling ability of the electrolyte, the new experimental swelling data, which reflects the passive swelling of the polymer for 30 minutes, can then be subtracted from the active swelling results shown in this report. Thus, the absolute active swelling results can be obtained.

Finally, due to the nature of the actuators used in the active swelling for the experiment, the polymer must be processed using Medipacs' proprietary processing technique before the results can be confirmed. It is expected that upon applying Medipacs' proprietary processing technique that the swelling will increase for every electrolyte. In fact, even the swelling rate of 0.1M citric acid, the best-swelling electrolyte for Medipacs' polymer, is expected to have a significant increase in swelling. This expectation is due to the fact that the Medipacs polymer actuators used in this report began to reach their maximum swelling limit, indicated because the polymer began to curl and bow on one side, during the 30-minute active swelling procedure in 0.1M citric acid.

Even if the electrolytes proposed in this report fail, in some way, to pass all of the recommended extra tests, they do provide an important insight into the target "ideal" electrolyte solution for Medipacs' polymer. Quite simply, an electrolyte solution that is free to donate hydrogen atoms to the system, but that is not naturally oxidized (has a negative standard electrode potential) is expected to have positive results. As another requirement, the electrolyte should not form a gas during the reaction, as sodium bicarbonate does.

5.1 Works Cited

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